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EPA (Environmental Protection Agency) Workshop on N2O Emission from Combustion (Durham, NC., February 13-14, 1986)

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EPA WORKSHOP ON N_2O EMISSION FROM COMBUSTION

(Durham, N.C., February 13-14, 1986)

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16. ABSTRACT The report summarizes the dialogue and interaction which took place during an EPA sponsored workshop addressing nitrous oxide (N2O) emissions from fossil fuel combustion. The workshop was held in Durham, NC, February 13-14, 1986. Prior research had identified N2O as a trace gas potentially contributing to depletion of stratospheric ozone as well as being a contributor to global climate change through the greenhouse effect. Prior studies also suggested that fossil fuel combustion was a major anthropogenic source of N2O emissions. The workshop was organized to assess the current understanding of combustion generated N2O emission and to assist EPA in formulating combustion research activities. The four technical sessions addressed: (1) N2O measurement, (2) N2O formation/destruction mechanisms during combustion, (3) emission source prioritization, and (4) emission control approaches. It appears that the most significant N2O emitters are utility and industrial boilers firing coal and heavy fuel oil. Mobile sources are a minor contributor to atmospheric N2O loading. Available field test data indicate a direct correlation between N2O and nitrogen oxide (NOx) emission rates, suggesting that combustion modifications for NOx control may also reduce N2O emission. The current data base and the understanding of N2O formation are insufficient to identify control strategies.

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Nitrogen Oxide (N_2O)	Stationary Sources	07B
Emission		14G
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ABSTRACT

This report is a summary of the dialogue and interaction which took place during an EPA sponsored workshop addressing nitrous oxide (N_2O) emissions from fossil fuel combustion. The workshop was held in Durham, North Carolina on February 13-14, 1986. Prior research studies had identified N_2O as a trace gas potentially contributing to depletion of stratospheric ozone as well as being a contributor to global climate change through the greenhouse effect. Prior studies also suggested that fossil fuel combustion was a major anthropogenic source of N_2O emissions. The workshop was organized to assess the current understanding of combustion generated N_2O emission and to assist EPA in formulation of appropriate combustion research activities. There were four technical sessions which addressed: (1) measurement of N_2O; (2) N_2O formation/destruction mechanisms during combustion; (3) emission source prioritization; and (4) emission control approaches. It appears that the most significant N_2O emitters are utility and industrial boilers firing coal and heavy fuel oil. Mobile sources are a minor contributor to the atmospheric N_2O loading. Available field test data indicate a direct correlation between N_2O and NO_x emission rates suggesting that combustion modifications for NO_x control may also reduce N_2O emission. The current data base and the understanding of N_2O formation processes are insufficient to identify control strategies. Workshop attendees suggested that further research be conducted to improve the data base and to better understand the chemical processes controlling N_2O formation and destruction.

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EXECUTIVE SUMMARY

The U.S. Environmental Protection Agency sponsored a workshop concerning nitrous oxide (N_2O) emissions from the combustion of fossil fuels which was held at the Sheraton University Center in Durham, N.C. on February 13-14, 1986. The workshop was designed to help EPA identify critical issues related to combustion emission of N_2O which would serve as the basis for developing an N_2O research program plan. This report is a summary of the dialogue and interaction which took place during the workshop.

Concern over nitrous oxide emissions is based on the facts that (1) N_2O participates in reactions which deplete ozone in the stratosphere, (2) N_2O is a greenhouse gas and, (3) atmospheric N_2O concentration is increasing. Nitrous oxide is one of several trace gases which participate in ozone depletion reactions. Ozone strongly absorbs ultraviolet radiation from the sun at wavelengths between 240 and 320 nm. If the stratospheric ozone concentration is decreased, increased quantities of this radiation, referred to as UV-B, will reach the Earth's surface with potentially serious effects on human health, agricultural productivity, and fisheries.

In addition to participation in ozone depletion reactions, there is concern for the fact that N_2O absorbs infrared (IR) radiation in wavelength ranges which are normally transparent in the atmosphere. This IR absorption process reduces cooling of the earth during the night. This is the greenhouse effect usually associated with CO_2.

The atmospheric concentration of N_2O was about 300 ppb in the late 1970's but is increasing at a rate of approximately 0.25 percent per year. The increasing concentration is of particular concern since there are no known atmospheric sinks for N_2O. In fact, the stratospheric lifetime of N_2O is estimated to be in excess of 100 years.

Nitrous oxide is emitted to the atmosphere from both natural and anthropogenic sources. As illustrated in Fig. ES-1, soil denitrification and ocean release account for about two-thirds of the ambient N_2O loading. It is believed that one of the major sources of anthropogenic N_2O is the combustion of fossil fuel. Since combustion generated N_2O is potentially controllable, the EPA and others are examining methods which may be effective in reducing N_2O emissions from combustion sources. It should be emphasized that the scope of the current workshop was limited to examination of combustion generated N_2O

TOTAL NATURAL: ≈ 0.3 Tmol/yr (from stratospheric removal models assuming no other sinks)

OCEANS: ≈ 0.1 Tmol/yr (from mean oceanic supersaturation of ≤4% and radon calibrated exchange models)

TERRESTRIAL: ≈ 0.2 Tmol/yr (by difference, includes soil sources and sinks)

ANTHROPOGENIC: ≈ 0.14 Tmol/yr (from observed rate of increase and box model calculations)

NOTE: 1 Tmol = 10^{12} gm moles

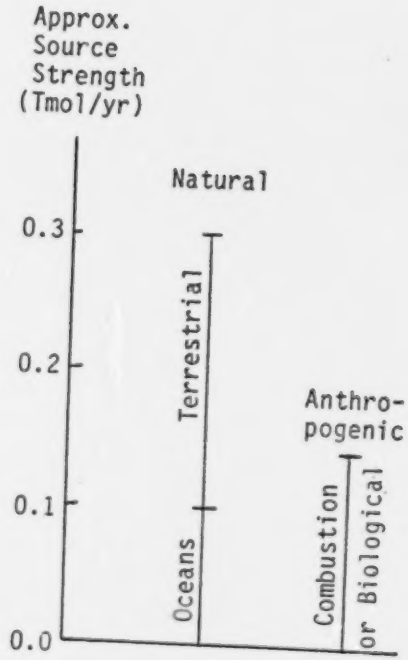


Figure ES-1. Estimated N_2O global fluxes
Source: Presentation by R.F. Weiss, Scripps Institution of Oceanography, (1986)

and did not address the impact of potential control strategies on ozone layer protection, global climate change, or human health. The workshop was organized to assist EPA in defining the critical combustion issues and in pointing to appropriate research actions to be taken.

The workshop was divided into five sessions - an introductory session containing an overview of the global N_2O situation, and four technical sessions which covered N_2O measurement techniques, N_2O formation/destruction mechanisms, source prioritization, and control approaches.

The introductory session began with an overview of EPA's risk assessment studies relative to global climate change. With the current levels of trace gases in the atmosphere, modification of the global climate is inevitable - even if current emission levels are drastically reduced. With current emission rates it is projected that the global surface temperature could rise by as much as 5°C over the next fifty years. This is as much as the temperature differential between the current level and that at the height of the Ice Age. The potential gravity of the situation is great, but is often overlooked by both researchers and the general public. It should be emphasized that N_2O is only one of several gases contributing to the climate change phenomena and that the global warming projections are the cumulative effect from all such gases.

Various studies of the global atmospheric budget have been performed, including present loading levels and projections of the sources and distribution of emissions. One such analysis indicates that the United States is currently the largest contributor to atmospheric N_2O due primarily to emissions from coal and heavy oil fired boilers. In the future the undeveloped countries are likely to be the leaders in emission rates. The results from this study are intended to focus the attention of research upon those areas which are identified to be the most significant emission sources. The results point primarily toward examining large, coal-fired industrial and utility boilers.

EPA is critically concerned with the quality assurance and quality control of their funded research activities, particularly of those data impacting policy and regulatory decisions. The first technical session of the workshop dealt with potential N_2O measurement techniques in order to define the appropriate techniques for different types of experiments, as well as to exchange information among the participants on potential sources of measurement

error. The majority of N_2O concentration data reported at the workshop was obtained by using gas chromatography (GC) with electron capture detection (ECD). Taking into account the state of development, precision, detection limit, and the cost of measurement, GC/ECD is an appropriate measuring technique for the majority of EPA funded research activities, including stack gas measurements. There are other measurement techniques which could be appropriate for other applications, but each measurement system must be adapted to the particular experiment being performed. Table ES-I shows some of the types of measurement systems which could be used for various experiments.

The second technical session examined the combustion chemistry controlling N_2O formation and destruction. Fig. ES-2 presents field test data on N_2O exhaust concentration from various boilers firing different fuels. These data clearly indicate a trend of decreased N_2O emission with decreased NO_x. A straight line correlation of these data indicates a constant N_2O:NO_x molar ratio of 22 percent. The control strategy implication of this data trend is that combustion modification techniques for NO_x reduction may also be effective in reducing N_2O emissions. One of the important workshop discussion topics was consideration of this trend. It was noted that essentially all of the data were taken from different units and did not examine N_2O emissions under normal and low-NO_x conditions. In the absence of such data, a control strategy based on implementing low NO_x control is not scientifically justifiable. That is to say, additional research is required to establish a control strategy. The need for additional R&D is amplified by two sets of pilot scale data indicating conflicting N_2O emission results. One set of data indicates that the N_2O:NO_x emission ratio remains constant as NO_x is reduced by combustion modification. The second set of data indicates that the exhaust N_2O concentration remains constant as the NO_x emission rate is reduced by a factor of six through application of staged combustion.

There was extensive discussion of chemical, mixing, and thermal phenomena which are important in controlling the N_2O formation and destruction processes. It was generally concluded that current knowledge does not provide a sufficient understanding of N_2O control in the combustion process. Many workshop participants felt that additional fundamental research to develop a "working hypothesis" of N_2O formation and destruction was an important first step in an EPA research program.

Table ES-I. Comparison of measurement systems for different applications

Measurements	Standards	Chromatography		FTIR	DIODE IR	NDIR
		ECD	N_2O/CO_2			
Ambient	X*	X	X			
Stack		X				X
Plumes		X	X	X	X	X
Flame					X	

*Standards available only for ambient measurements. Standards are needed for all measurements.

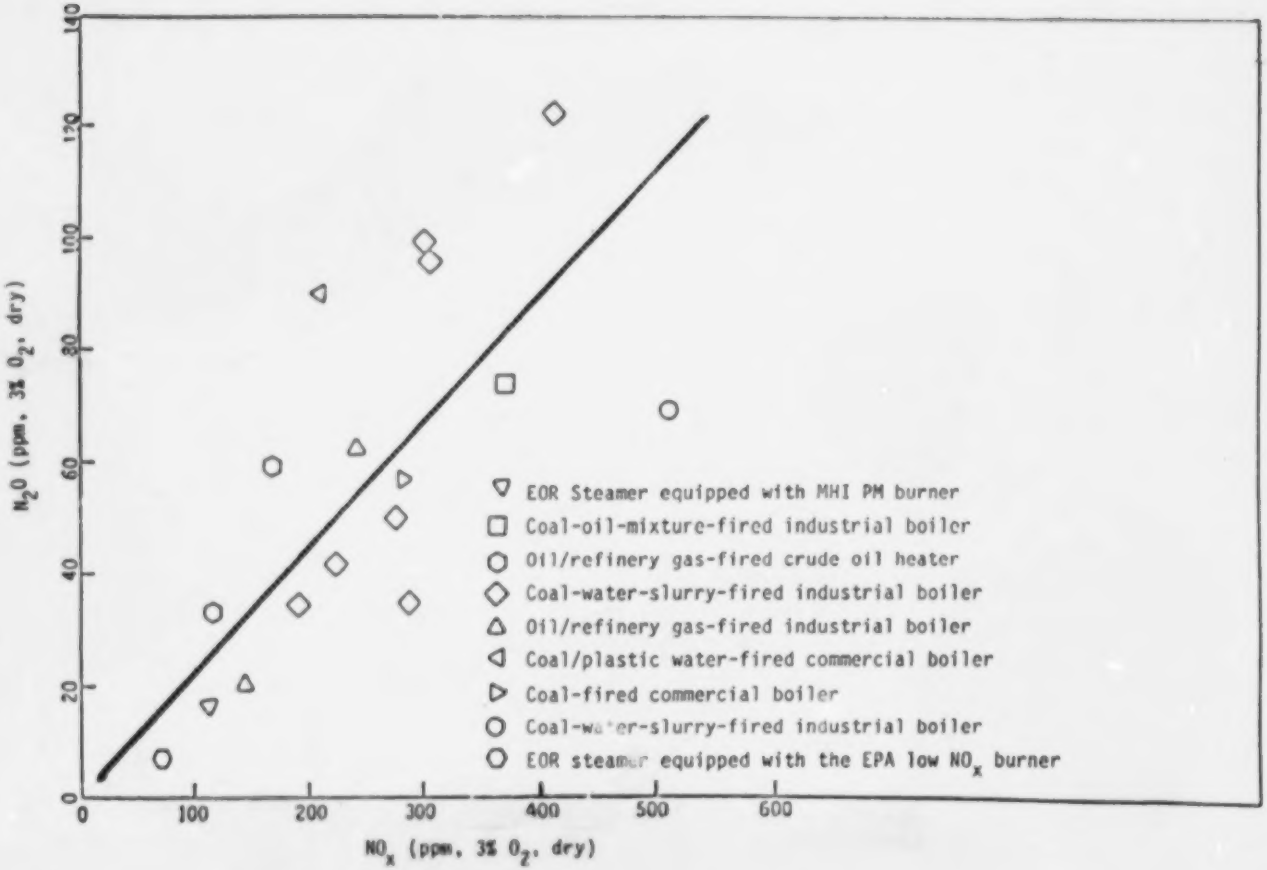


Figure ES-2. N_2O emissions from combustion sources as a function of NO_x emission
Source: "Environmental Assessment of an Enhanced Oil Recovery Steam Generator Equipped with a Low-NO_x Burner, Volume 1. Technical Results," EPA Report No. 600/7-86-003a, 1986.

The second session also provided important information defining the dominant sources of N_2O emissions. Fig. ES-3 shows results from utility boiler field tests in which the $N_2O:CO_2$ molar ratio in the boiler exhaust is correlated with the nitrogen to carbon molar ratio in the fuel being fired. This figure suggests a constant fractional conversion of fuel bound nitrogen to N_2O, which implies that coal and heavy oil fired boilers are the most important N_2O emission sources. This trend further supports the analysis which defined large industrial and utility boilers as the largest contributors to anthropogenic N_2O emissions.

The third technical session was focused on mobile versus stationary source emissions of N_2O and was included in the workshop to aid EPA in determining priorities for R & D activities. The global projections referred to earlier indicate N_2O emission growth in the third world as well as in the U.S. - both in the energy sector and in the transportation sector. It is important from both a U.S. EPA and a global perspective to define whether one sector is much more important than the other, or whether it is necessary to address both areas.

As shown in Table ES-II, there are limited data available from mobile sources. However, the available data show a large variation in emission rates - from 5 to 147 mg N_2O per mile. Assuming an average emission rate of 100 mg/mile and estimating the total vehicle miles travelled in the U.S. at approximately 1.6×10^{12}* per year, the total annual U.S. N_2O emission rate from mobile sources is on the order of 1.6×10^5 metric tons. It has been estimated that the total anthropogenic N_2O emission rate is approximately 3.0×10^6 metric tons per year which implies that U.S. mobile sources account for only about 5.5 percent of the anthropogenic total.

It is also noted in Table ES-II that the N_2O emission rate from non-catalyst equipped cars was only 5-6 mg/mile - an order of magnitude less than the assumed average emission rate used in the above calculation. Since it is unlikely that other nations, such as third world countries, will require automotive catalysts, it appears that the mobile source sector will remain an insignificant contributor to atmospheric N_2O loading. Before a firm conclusion may be reached, however, it is essential that the N_2O emission rate data

*Motor Vehicle Facts and Figures, 1984, Motor Vehicle Manufacturers Association, ISSN #0272-3995, p.52.

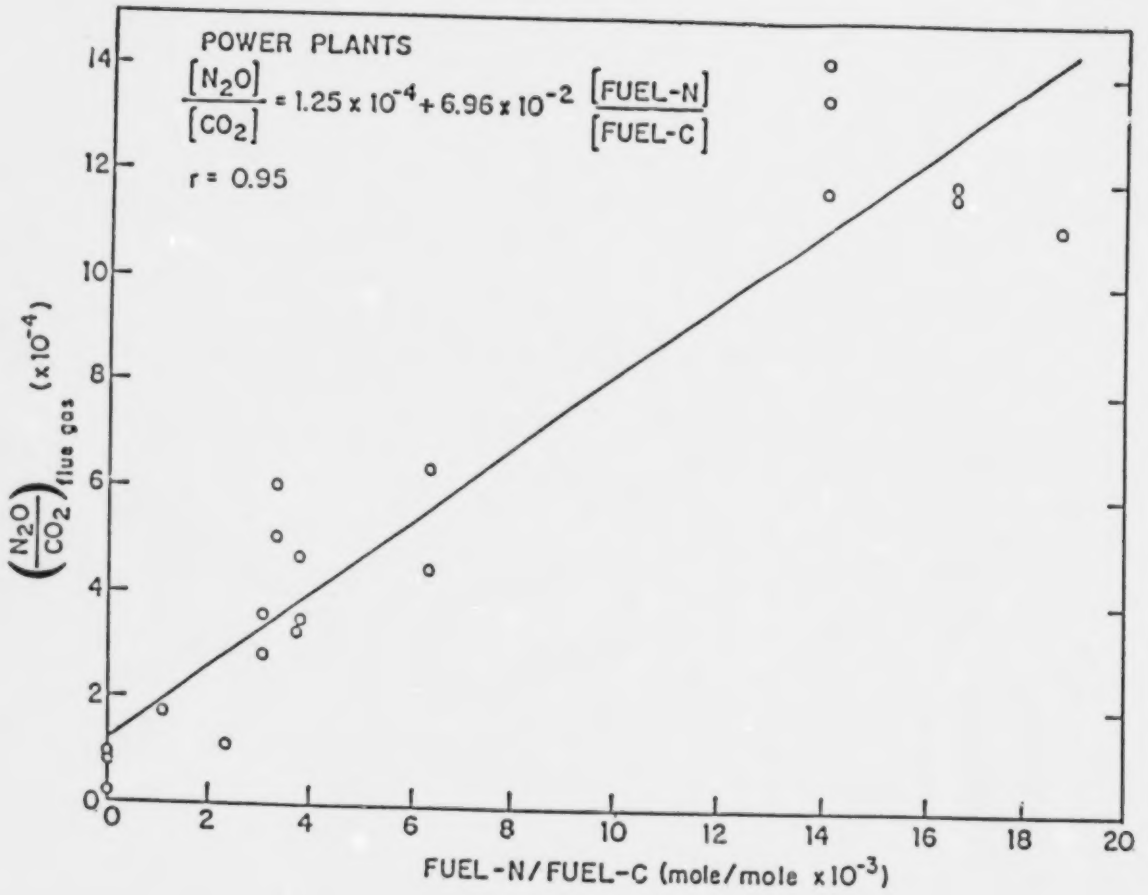


Figure ES-3. Relationship between N_2O emissions and fuel-nitrogen contents of natural gas, no. 6 fuel oil and coal fired combustion systems
Source: Wofsy et al., Harvard Univ., (1986)

Table ES-II. N_2O emission data for various vehicle types
Sources: See references 1-6.

VEHICLE TYPE	NO. OF SAMPLES	N_2O EMISSION RATES (mg/mi)
1. Non Catalyst Car	1	5 - 6
2. Catalyst Cars	22	7 - 137
3. Diesel Trucks/Buses	4	31 - 147
4. Gasoline Trucks	2	48 - 97

base be significantly expanded - particularly for non-catalyst equipped vehicles. To expand that data base it was suggested that N_2O measurements be incorporated into existing vehicle emission monitoring and certification testing. With regard to expansion of the non-catalyst equipped auto data base, it was suggested that other countries could assume responsibility through international cooperation coordinated by the United Nations.

Results from field tests of different stationary sources fired with different fuels are shown in Fig. ES-4. These results incorporate those presented earlier in Fig. ES-2, showing a general correlation between N_2O and NO_x emissions. With the expanded data set there is a substantial increase in data scatter underlining the need for additional research before reliable emission factors can be developed.

The purpose of the final technical session was to identify combustion control approaches or strategies which could be used to reduce N_2O emissions. Since many potential control methods had been considered during the previous workshop sessions, this session was mainly a summary discussion. The concept of reburning was introduced as a possible NO_x control strategy which could be applicable to N_2O emission control as well. However, it was emphasized that not all NO_x controls would automatically be effective in reducing N_2O emissions, and that careful study must be made to determine each method's effectiveness. "Piggybacking" of N_2O measurements onto current test programs was suggested as a cost-effective method to augment the N_2O emission data base.

The various workshop sessions identified many important data trends which may be used to form working hypotheses but also underlined the fact that the existing data base was insufficient to reach scientifically defensible conclusions. By way of summary, it would appear that N_2O emissions from combustion of nitrogen bearing fuels is far greater than from "clean" fuels. Mobile sources appear to be negligible N_2O emitters relative to stationary sources, but the data base for mobile sources is extremely limited (particularly for vehicles without catalysts). The available stationary source field data show a direct correlation between NO_x emissions and N_2O emissions. This indicates that installing low-NO_x burners or other NO_x control technologies <u>may</u> also be effective for N_2O control. It should be emphasized, however, that some pilot-scale results are in direct conflict with that indication. In fact, one of the main workshop conclusions is a call for additional fundamental and bench-scale research to clarify this discrepancy.

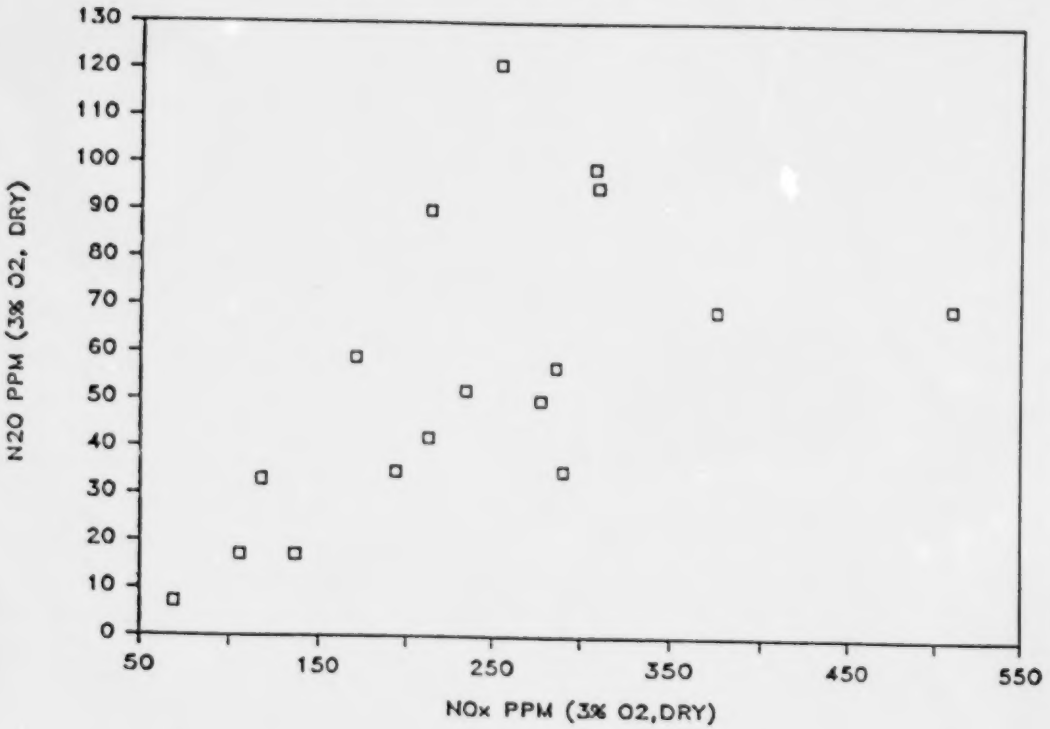


Figure ES-4. N_2O and NO_x emissions from various sources
Source: C. Castaldini, Acurex, (1986)

Depletion of the ozone layer and the greenhouse effect are clearly important environmental concerns but immediate regulatory response appears unlikely. On that basis, prudent programmatic actions could include:

- Addition of N_2O measurement in any existing field evaluation programs to help build the data base,
- Initiation of fundamental combustion research to identify how N_2O emissions are impacted by NO_x control combustion modifications, and
- Formation of a working group to coordinate research activities at EPA, NASA, DOE, and NOAA.

These actions could be accomplished with minimal resources and would place the EPA in a better position if control technology or regulatory actions were required in the future.

INTRODUCTION

This report provides a summary of a workshop sponsored by the U.S. Environmental Protection Agency (EPA) to address atmospheric emission of nitrous oxide (N_2O) from combustion of fossil fuels. The workshop was held at the Sheraton University Center in Durham, North Carolina, on February 13-14, 1986. Organizational responsibilities were assumed by EPA's Air and Energy Environmental Research Laboratory (AEERL), Combustion Research Branch, with support from Energy and Environmental Research Corporation (EER).

The objective of the N_2O workshop was to help EPA identify the critical issues related to N_2O combustion emissions. Once the issues are identified, EPA will be able to begin development of an effective research program plan.

Over the past several years it has become evident that the atmospheric concentration of N_2O is increasing at a rate of approximately 0.25 percent per year. Nitrous oxide is one of several trace gases which participate in ozone depletion reactions in the stratosphere and which absorb IR radiation to create what is known as the greenhouse effect. There is normally an abundance of ozone in the stratosphere. If that normal abundance is depleted, increased amounts of UV-B radiation will reach the Earth's surface, causing potential health effects such as melanoma. The environmental impact of such global climate change is potentially of unprecedented proportion with respect to Earth surface warming. In recognition of the problem, EPA is participating in both domestic and international programs that will:

(1) assess the atmospheric science and effects of stratospheric ozone depletion;

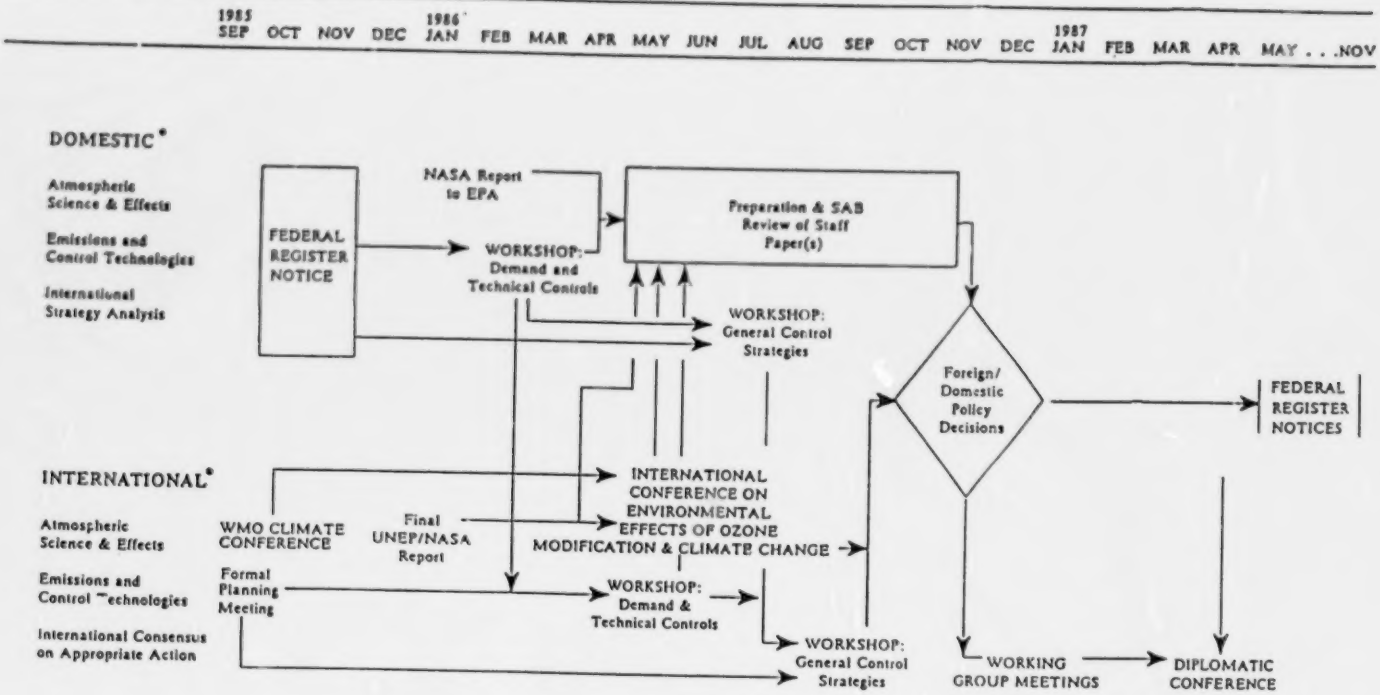
(2) evaluate pollutant emission release rates and potential control technologies; and

(3) develop an international strategy for mitigating the potential impact.

Fig. 1 presents the schedule of activities for EPA's stratospheric ozone protection program pointing toward an international consensus on appropriate action in mid-1987. The N_2O workshop summarized in this report is a direct line item in the EPA schedule under domestic activities--emissions and control technologies.

Figure 1

ACTIVITIES RELATED TO EPA'S STRATOSPHERIC OZONE PROTECTION PROGRAM


1985 SEP OCT NOV DEC 1986 JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC 1987 JAN FEB MAR APR MAY . . . NOV
DOMESTIC*
Atmospheric Science & Effects
Emissions and Control Technologies
International Strategy Analysis
FEDERAL REGISTER NOTICE
NASA Report to EPA
WORKSHOP: Demand and Technical Controls
Preparation & SAB Review of Staff Paper(s)
WORKSHOP: General Control Strategies
Foreign/ Domestic Policy Decisions
FEDERAL REGISTER NOTICES
INTERNATIONAL*
Atmospheric Science & Effects
Emissions and Control Technologies
International Consensus on Appropriate Action
WMO CLIMATE CONFERENCE
Final UNEP/NASA Report
INTERNATIONAL CONFERENCE ON ENVIRONMENTAL EFFECTS OF OZONE MODIFICATION & CLIMATE CHANGE
Formal Planning Meeting
WORKSHOP: Demand & Technical Controls
WORKSHOP: General Control Strategies
WORKING GROUP MEETINGS
DIPLOMATIC CONFERENCE

* STUDIES ONGOING IN ALL CATEGORIES TO SUPPORT MAJOR EVENTS

To date, the primary research activities related to stratospheric ozone protection have concentrated on the atmospheric "Science and Effects" area. Those studies have shown that the atmospheric concentration of N_2O "is increasing at about 4 x 10^6 tons N per year from a 1982 base of about 1515 x 10^6 tons N."[7] There are no known major sinks for N_2O once it enters the stratosphere and as a result, its atmospheric life time is greater than 100 years.[8,9] The available data base is still meager, but understanding of the atmospheric N_2O budget has improved over the past decade. These budgets indicate that the anthropogenic N_2O flux is approximately 50 percent of the natural source strength. Dominant natural emission sources include release from the oceans and release from soils. The anthropogenic release rate is based on the observed rate of increase in atmospheric N_2O concentration and model calculations. It is believed that one of the major anthropogenic sources of N_2O emission is combustion of fossil fuel. From an international policy perspective, combustion generated N_2O is an important consideration in that it is a potentially controllable source.

The available data base describing N_2O emission rates from combustion sources is more limited than the overall atmospheric data base. Several groups have measured the N_2O concentration in combustion exhausts. These measurements were generally single data points from specific boilers in their normal operating condition[10,11] or were peripheral measurements in NO_x control studies.[12] Such data are not sufficient to establish reliable emission factors and are clearly insufficient for identifying potential control strategies.

WORKSHOP PLANNING AND FORMAT

Planning for the workshop began by identifying key individuals or groups active in the N_2O emission research area. Three groups of potential workshop participants were identified:

(1) Scientists actively involved in N_2O research with primary focus in the atmospheric chemistry area;

(2) Scientists actively involved in combustion chemistry of nitrogen species, but with limited data on N_2O emissions or control;

(3) Government officials charged with development of policy positions and/or development and execution of research programs.

Each of these three groups provide a different perspective on the N_2O emission problem and obtaining input from each group was an important factor in achieving the workshop objective. The number of participants was kept to a minimum (20-30 people) in the belief that a small meeting would be conducive to active interchange of current data and personal opinions.

In December, 1985, letters of invitation were mailed to several of the targeted individuals. Responses from this invitation letter along with follow-up telephone calls were used to establish the workshop meeting dates and to help finalize the list of participants. (A sample copy of this invitation letter and a list of participants is included in Appendix A.)

Since EPA's objective would best be gained through active discussion among the participants, an informal atmosphere was encouraged. The workshop was divided into five sections: an introductory section in which overview information on N_2O and the greenhouse effect was presented, and four technical sessions. The four technical sessions covered:

I. N_2O measurement techniques

II. N_2O formation/destruction mechanisms

III. Source prioritization

  A. Mobile sources

  B. Stationary sources

IV. Control approaches

In late January, 1986, a second letter was sent to the chosen participants. The letter contained a tentative agenda and outlined a series of critical issues to be addressed in each technical session. (A copy of this second letter and agenda is provided as Appendix B.) Each session had a discussion leader who made a brief presentation that outlined the critical issues of that session and provided his opinion on the issues. The floor was then opened for discussion and the session leader solicited input from individuals with specific knowledge in the area. At the end of each session, a worksheet listing the session's critical questions was provided to each participant. The participant then responded in writing to the questions, giving his opinion on the subject.

OPENING REMARKS AND BACKGROUND PRESENTATIONS

Mr. R. P. Hangebrauck, Director of EPA's Energy Assessment and Control Division, opened the meeting with a welcome to the participants. Following Mr. Hangebrauck's remarks, Mr. R. E. Hall, Chief of EPA's Combustion Research Branch (CRB) provided a brief overview of CRB's past involvement in N_2O data gathering. He explained that CRB has maintained an active R&D program in the area of NO_x control by combustion modification. One CRB sponsored study with Acurex Corporation was designed to provide comprehensive environmental assessments of stationary combustion sources modified to control NO_x emissions. As part of that study, the N_2O emission rate was measured from a variety of combustion sources. Those data, obtained as a side issue in the NO_x control evaluation, represents a substantial portion of the available N_2O combustion emission data base. An important aspect of these data was that exhaust N_2O concentration was found to be a constant percentage of the NO_x concentration.

After a brief discussion of the meeting format by Mr. J. A. McSorley (CRB) and Dr. W. S. Lanier of Energy and Environmental Research Corporation (EER), the meeting was turned over to Mr. Dennis Tirpak of EPA's Office of Policy, Planning and Evaluation (OPPE), and Dr. Mike Kavanaugh, a contractor to OPPE.

Mr. Tirpak's presentation provided an overview of risk assessment studies being performed by EPA relative to global climate change. As background information, copies of a January, 1986 NASA report titled "Present State of Knowledge of the Upper Atmosphere: Processes that Control Ozone and Other Chemically Important Trace Gases" were provided to participants. This report is an excellent review of the processes responsible for the overall climate change process. Section III of that report entitled "The Problem" is paraphrased herein to place N_2O emissions into perspective.

Fig. 2 illustrates the standard definitions of the troposphere, stratosphere, and mesosphere in terms of temperature variation with altitude and also shows the average ozone concentration distribution (molecules/cm^3). The peak ozone concentration occurs in the lower stratosphere between 20-25 km altitude. This peak concentration is never more than about 10 parts per million by volume.

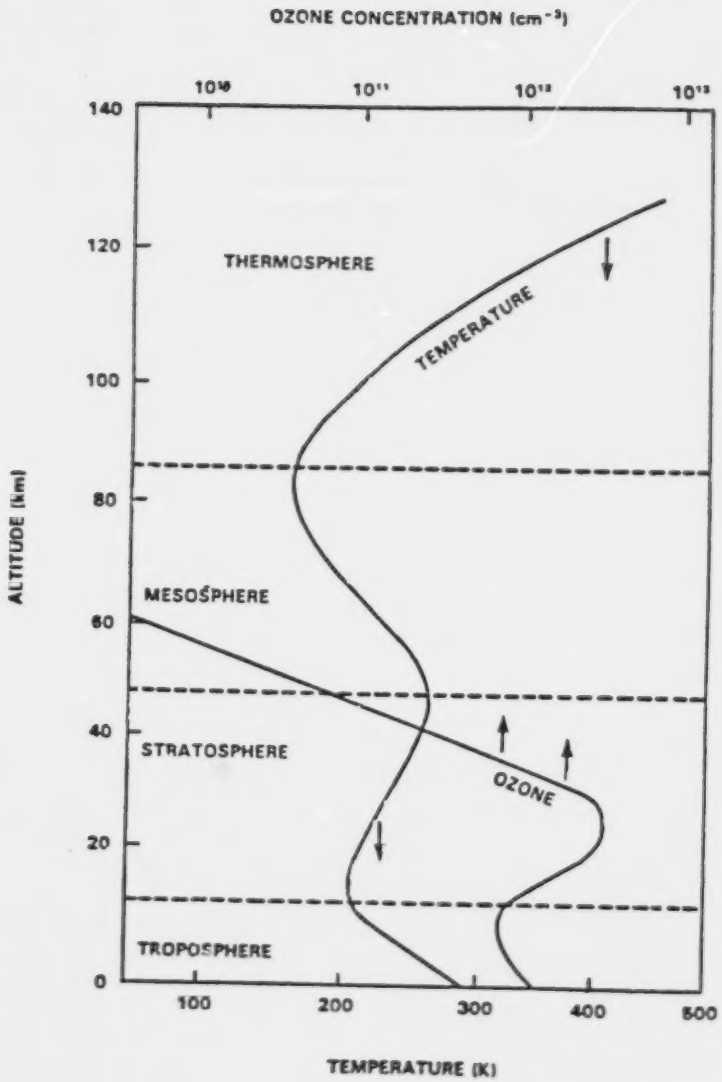


Figure 2. Temperature profile and ozone distribution in the atmosphere

Ozone strongly absorbs ultraviolet radiation from the sun at wavelengths between 240-320 nm. If this radiation, referred to as UV-B, is allowed to reach the ground in significant amounts, serious effects on human health, agricultural productivity and fisheries can result. Absorption of solar radiation in the 200-320 nm wavelength range (mainly by ozone) is also the source of heating in the stratosphere. Thus the vertical distribution of ozone plays the primary role in determining the temperature distribution and consequent motions of the stratosphere.

Solar radiation transmitted through the atmosphere is partially reflected and partially absorbed at the Earth's surface. This surface absorbed radiation heats the troposphere from below and can result in unstable, rapid convective vertical motions such as in cumulus clouds. Because ozone provides the main heat source for the stratosphere, its vertical distribution plays the primary role in determining the temperature structure and consequent motions of the stratosphere. Less stratospheric ozone implies less absorption of solar radiation in the stratosphere, allowing more solar radiation to reach the surface. This effect alone tends to warm the surface. Less stratospheric absorption of solar radiation, however, reduces stratospheric temperature and therefore reduces infrared radiation from the stratosphere to the troposphere. This effect, taken alone, tends to cool the surface. If stratospheric ozone is uniformly reduced, these two effects almost cancel each other with slight cooling of the troposphere generally predicted. The radiative balance depends on the altitude of ozone reduction as well as changes in column amounts of ozone. Ozone changes in the lower stratosphere and upper troposphere are more significant than changes in other regions of the atmosphere in causing surface temperature modifications. Latitudinal variations are also important. Spatially uniform O_3 reduction will result in greater changes in radiative fluxes at higher latitudes than in the tropics.

The concentration of ozone in the atmosphere represents a balance of formation and destruction processes. UV radiation at less than 242 nm is sufficiently energetic to dissociate O_2 into two oxygen atoms which rapidly react with O_2 to form ozone. This ozone absorbs UV radiation in the 200-320 nm wavelength region causing dissociation into O_2 and an O atom. Thus, a chain process is established with oxygen atoms alternately attached to O_2 forming O_3, and then detached to reform O_2 and O. This chain is terminated when an O atom reacts with an O_3 molecule to reform two O_2 molecules. The

concentration of O_3 is determined by the length of the chain before the $O + O_3 \rightarrow 2O_2$ reaction occurs.

The addition of N_2O to the troposphere and stratosphere influences the ozone chain and the overall radiative balance in two ways. In the troposphere, N_2O absorbs infrared radiation in wavelength ranges which are normally transparent. This IR absorption process reduces cooling of the earth during the night. This is the greenhouse effect usually associated with CO_2. In the stratosphere, N_2O can react with excited state oxygen $O(^1D)$ to form NO. Data indicate that NO_x emitted to the troposphere is not transported to the stratosphere and that N_2O is the dominant source of odd-nitrogen in the stratosphere. NO_x species from N_2O then participate in a catalytic cycle including the two reaction set:

$$\begin{array}{rl} & NO + O_3 \rightarrow NO_2 + O_2 \\ & NO_2 + O \rightarrow NO + O_2 \\ \hline \text{Net} & O + O_3 \rightarrow O_2 + O_2 \end{array}$$

This two reaction set is referred to as catalytic since, at the end, the NO molecule is again available to continue converting O and O_3 back to O_2. A similar process of absorbing IR radiation and catalytic participation in a net $O + O_3$ reaction exists for chlorofluorocarbons (CFCs), which also deplete the stratospheric ozone layer.

An important reason for concern is that the ambient concentrations of many greenhouse gases are increasing. Fig. 3 shows the variation in CO_2 concentration over the past 27 years. Despite the large seasonal variation, the mean concentration is clearly increasing with time. Other important greenhouse gases include N_2O, CFCl1, CFCl2, and methane. Fig. 4 shows that the concentration of each of these species is increasing with time. The primary source of this temporal increase is human activity which accompanies economic growth. The growth of CO_2 concentration is primarily attributable to fossil fuel combustion. The growth of N_2O concentration is attributed to increased use of nitrogenous fertilizers and the combustion process. Table I presents the projected annual growth rates in concentrations for important greenhouse gases as compiled by several different organizations. Due to its long atmospheric lifetime, the concentration of N_2O is expected to increase from its current level of about 304 ± 2 ppb and eventually reach about 400 ppb.

Mr. Tirpak presented Fig. 5 to illustrate the surface temperature rise (T_s) effect of various trace gases relative to CO_2 assuming continued

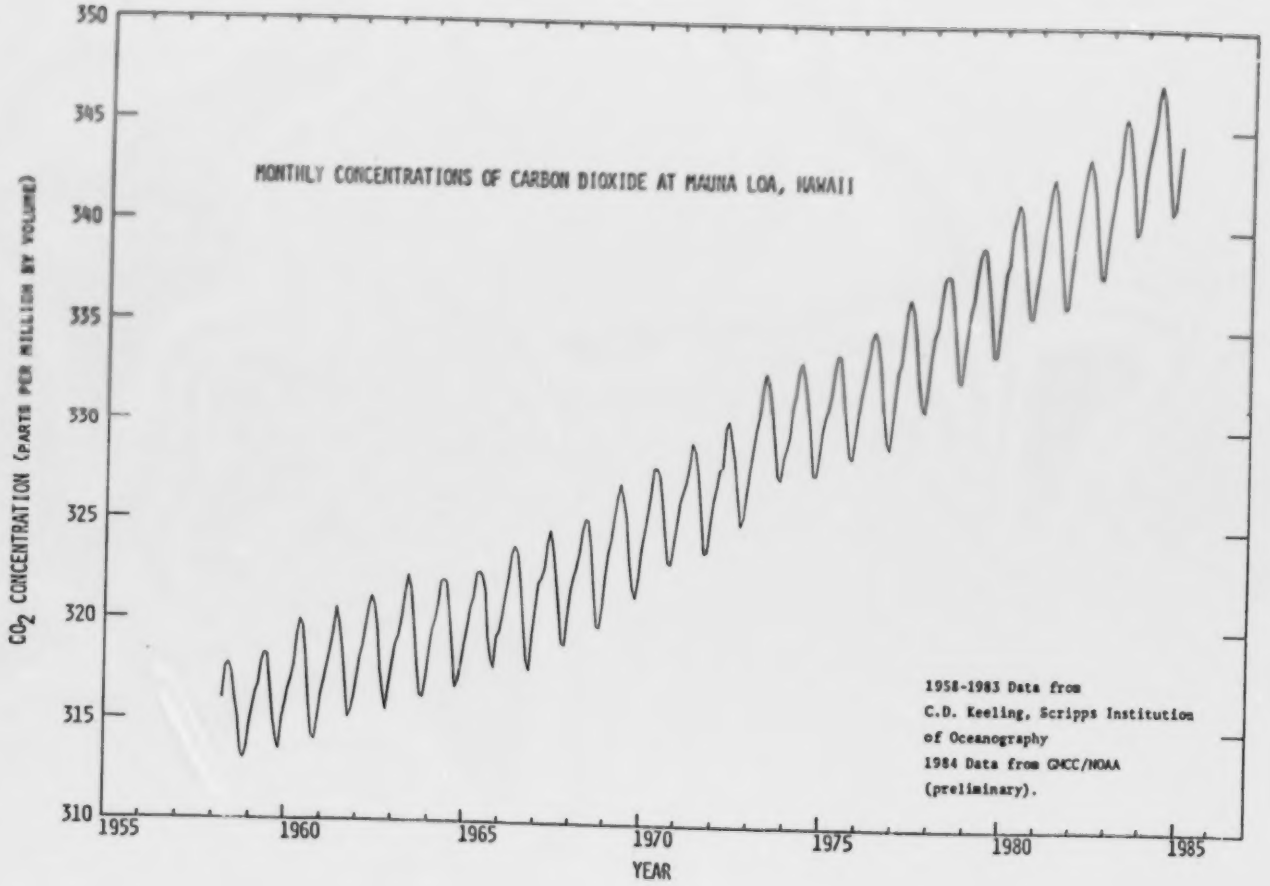
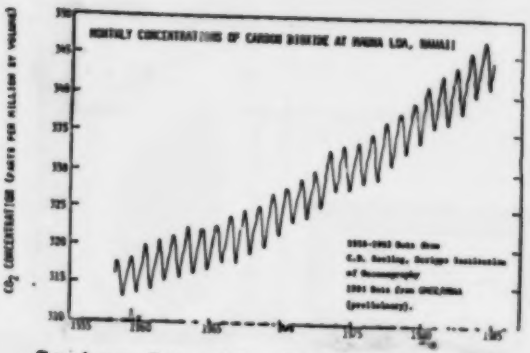
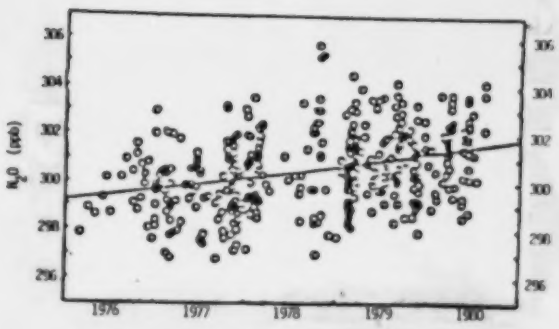


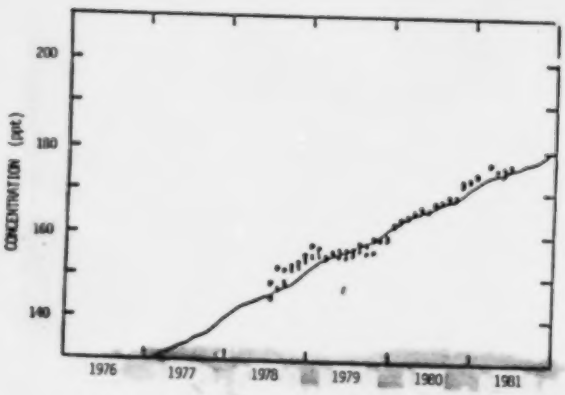
Figure 3. Monthly concentrations of carbon dioxide from 1958 to 1985



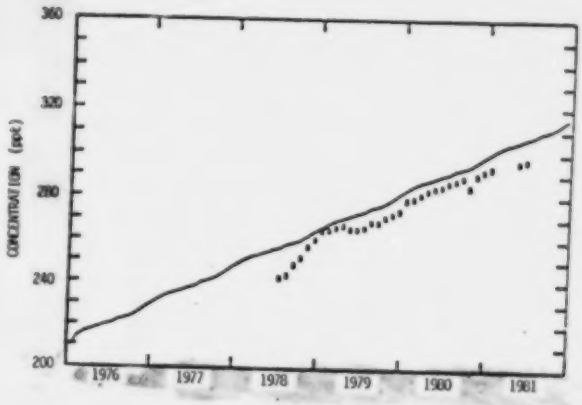
Carbon Dioxide Concentrations
Source: NOAA



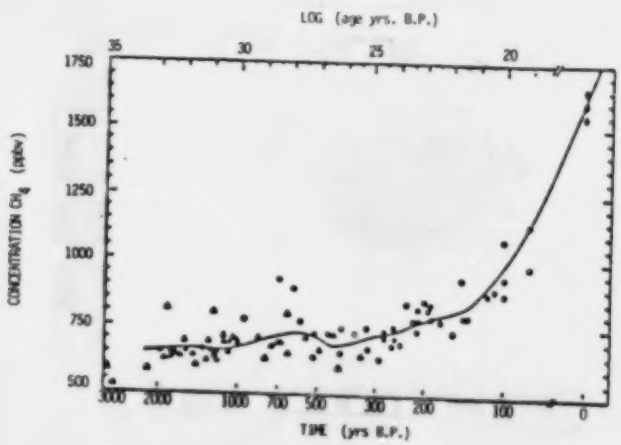
Nitrous Oxide Concentrations
Source: Weiss (1981)



CFC11 Concentrations
Source: Cunnold et al. (1983a)



CFC12 Concentrations
Source: Cunnold et al. (1983b)



Methane Concentrations
Source: Rassmussen and Khalil (1984)

Figure 4. **Measured trends in trace gases**
(Presentation by Tirpak, actual source of data unknown)

Table I. Projected annual growth rates in concentrations for various gases

INCREASES IN GASES ARE EXPECTED TO ACCOMPANY ECONOMIC GROWTH

	Projected annual growth rates in concentrations from 1980 to 2030					
	NAS	Cicerone (NCAR)	Wuebbles (LLNL)	RAND	ICF	Atmospheric Litetime (years)
Carbon Dioxide	0.50%	0.56%	0.56%	----	----	2
CFC11	-----	3.6%	-----	4.7%	4.9%	75
CFC12	-----	3.7%	-----	3.9%	4.9%	110
Methane	1.4%	0.7%	1.0%	----	----	5 to 10
Nitrous Oxide	0.25%	0.4%	0.25%	----	----	120
Minor trace gases						
SO2	-----	0%	-----	----	----	
F14	-----	2.9%	-----	----	----	0.001
F116	-----	3.2%	-----	----	----	> 500
CFC22	-----	5.4%	-----	6.7%	7.5%	> 500
CFC13	-----	4.3%	-----	----	----	20
Methylene Chloride	-----	3.8%	-----	----	----	400
$CHCl_3$	-----	2.2%	-----	----	----	0.6
Carbon Tet.	-----	1.7%	-----	2.3%	----	0.6
Methyl Chloroform	-----	4.7%	-----	2.9%	----	50
Halon 1301	-----	3.2%	-----	9.9%	----	6.5
C2H2	-----	1.0%	-----	----	----	110
						0.3

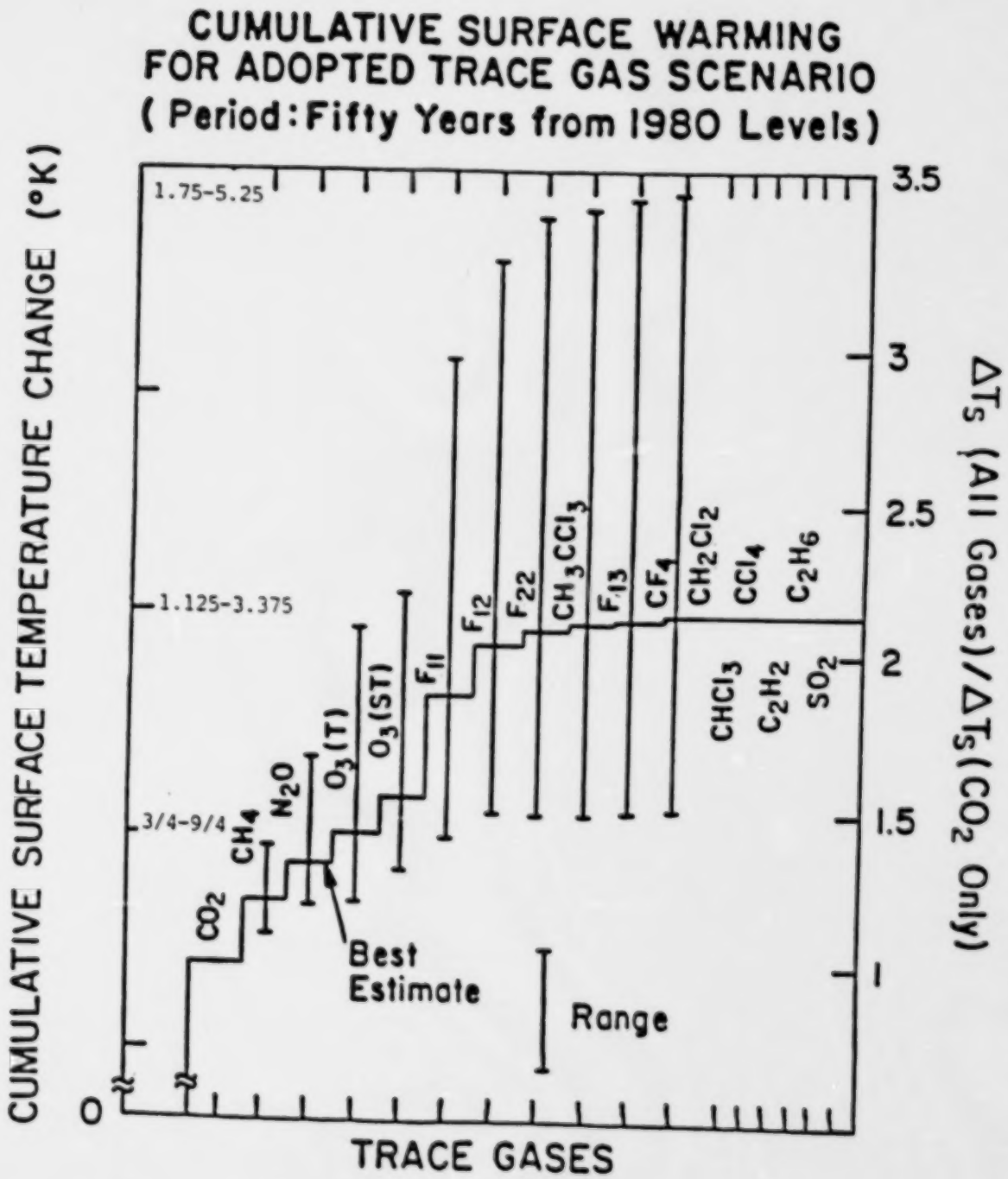


Figure 5. Cumulative surface warming for adopted trace gas scenario.

Ramanathan, V., et al., 1985. "Trace Gas Trends and Their Potential Role in Climate Change, "Journal of Geophysical Research."

concentration growth over the next 50 years (from a 1980 base). As shown, the best estimate line indicates that the cumulative T_s influence of trace gas is of equal importance to that of CO_2 and that over this 50 year period the Earth's surface temperature is expected to rise between 1.5 and 3.5°C. Fig. 6 illustrates the projected global temperature rise and shows that the largest increase in surface air temperature is expected to occur in the polar regions.

An important consequence of the long life of these trace gases is that global climate change cannot be prevented--even if emissions are totally terminated. The effects are quasi-irreversible and a "wait and see" strategy implies significant change.

It is extremely difficult to convey concern about these projected changes in global climate to the general public. According to Mr. Tirpak, there is public confusion over whether the Earth is getting hotter or colder, and general apathy over a projected problem that may not have any visible effect until somewhere between the years 2030-2100. Moreover, the perceived public attitude is a general feeling of "Who cares if it gets hotter by a few degrees or if the sea rises by a few feet?"

Mr. Tirpak's response to the perceived public attitude was to show the interrelation between climate change and the more immediate problem of acid rain. In the United States, there is a direct relation between change in temperature and percentage change in residential and commercial electricity sales with a 1°C temperature rise increasing electricity sales by 8-10 percent. This, in turn, results in a direct increase in SO_2 and NO_x emissions which are the primary acid rain precursors. There are also direct impacts of climate change on acid rain considerations. For example, increased air temperatures result in increased emissions of S, H^+, and NH_3 from soils and more rapid oxidation of SO_2 and NO_x to sulfates and nitrates. Other climate change phenomena with acid rain related impacts were also examined. (See Table II.)

The impact of ambient temperature increases of the order predicted in Fig. 6 is placed in perspective by examining historic trends. At the height of the Ice Age, the ambient temperature is estimated to have been only 5°C less than the current temperature level. The potential impact of the greenhouse effect is to raise the ambient temperature by as much as 5°C over the next 50 years.

Mr. Tirpak closed his presentation by briefly addressing the two short-

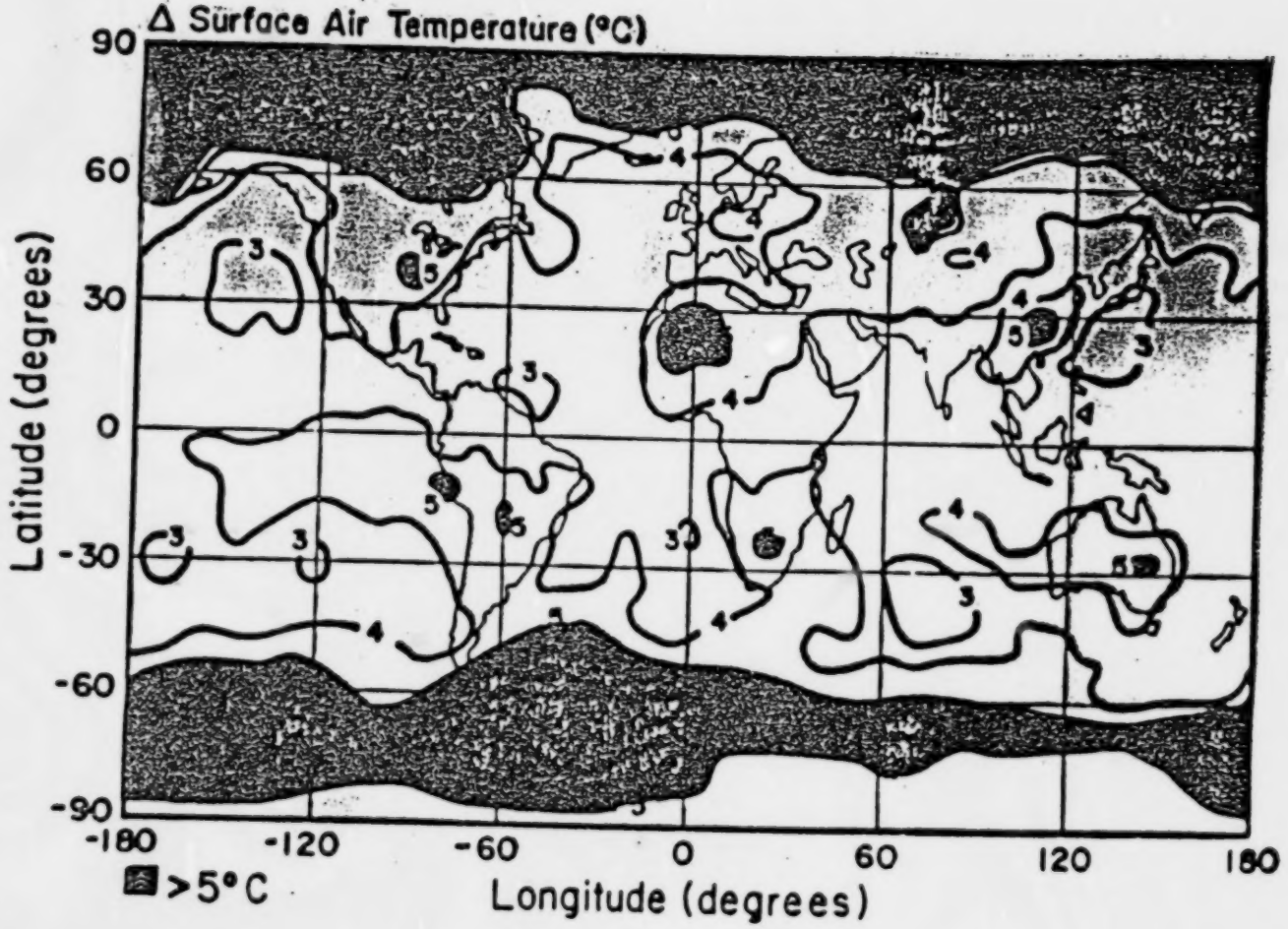


Figure 6. Projected global temperature rise

Table II. Climate change and acid rain impacts

Climate Change	Acid Rain Related Impact	Potential Implications
Increased Air Temperatures	Increased emissions of S, H^+ and NH_3, from soils	Potential anthropogenic emission reductions partially nullified
	More rapid oxidation of SO_2 and NO_x particularly in northern latitudes	Decreased importance of long range transport of SO_4 and NO_3 ions
Increased Water Temperatures	Increased S emissions from oceans	Increased importance of marine sulfur emissions along coastal areas
Changed Precipitation	Changed scavenging rates for atmospheric SO_4 and NO_3	Altered importance of long-range sources
	Changed seasonal and annual average deposition of SO_4, NO_3, and H^+	Altered impacts on aquatic system and forests

Table II. Climate change and acid rain impacts (continued)

Climate Change	Acid Rain Related Impact	Potential Implications
Changed Precipitation (continued)	Changed winter snow pack	Altered vulnerability of aquatic life during spring snow melt
	Altered frequency of wet days	Changed degradation rates for materials
Increased Ground Wetness	Increased emissions of S. N. NH_3 from soils	Anthropogenic emission reductions partially nullified
Increased Humidity	Increased production of lightning generated NO_x	Anthropogenic NO_x emissions decreases partially nullified
Changed Cloud Cover at Different Altitudes	Increased natural NO_x emissions from lightning	Changes in fertilization of high forests altitude

Table II. Climate change and acid rain impacts (continued)

Climate Change	Acid Rain Related Impact	Potential Implications
Changed Cloud Cover at Different Altitudes (continued)	Changes in cloudwater impaction at high altitudes	
	Changes in aqueous phase oxidation rates for SO_2 and NO_x	Altered significance of long rate transchanges
Increased Number of Days With Temperatures Above 0°C	Increased natural emissions Lengthened growing season	Changed food production
Increased Number of Days Without Frost	Changed significance of frost as a mechanism for forest damage	Potential decrease in forest impacts associated with forest and overfertilization by atmospheric nitrogen

Table II. Climate change and acid rain impacts (continued)

Climate Change	Acid Rain Related Impact	Potential Implications
Increased Dryness in Interior U.S. and Seasonal Changes and Frequency of Drought	Increased importance of dry deposition	Altered impacts on aquatic systems and forests
	Increased amount of Ca and Mg dust/particles	
	Increased pH of rainfall	
Increased Atmospheric CO_2	Increased fertilization of forest and crops - potential changes in demand for other nutrients including S and N	May negate possible forest productivity declines in some areas

term objectives of EPA's global climate change program. The first objective is to work with domestic and international groups to build the required understanding and institutional capability to address the problem. The second objective is to perform additional analyses to assure that EPA actions don't inadvertently speed up the rate of climate change. In the longer term EPA will follow an institutional and scientific agenda which is reflected in part by the various workshops and conferences defined earlier in Fig. 1.

Following Mr. Tirpak's remarks, Dr. Mike Kavanaugh presented initial results of global projections for N_2O and CO emission from combustion sources. The study was designed to assess the relative contribution of combustion sources to other sources, types of combustion sources, and different global regions to the atmospheric loading of N_2O and CO. Results of the study are intended both for use by atmospheric chemistry modellers and to focus future research by identifying important combustion emission sources, the regional distribution of emissions, and the relative source contributions.

The study approach began by dividing the world into six (6) geopolitical divisions. These divisions are shown in Fig. 7 and include:

(1)	United States	(USA)
(2)	Western Europe and Canada	(WEC)
(3)	Pacific Hemisphere	(PAC)
(4)	USSR	(USSR)
(5)	China	(CHINA)
(6)	Rest of World	(ROW)

Next, combustion was divided into five fuel types: coal, oil, gas, wood, other; and four sectors of fuel use: household, utilities, industries and transportation. Annual emissions were estimated by multiplying a measure of activity level by an emission coefficient. The activity level represents global estimates of market and non-market energy use divided according to region, sector, and year. The emission coefficients are taken from emission factors segregated by region, sector, and year (where possible). Projected emissions were calculated for the years 1960, 1975, 2000, and 2025.

There are many projections of future global market energy use with significant variations in the projections. Table III represents the median of several such projections and presents market energy use patterns for the six regions for the four evaluation years. Table IV presents the projected market energy use patterns for the United States divided by year according to

Figure 7. Global geopolitical divisions

Table III. Global market energy use by region

(QUADRILLION BTUS)

THE MEDIAN SCENARIO

	1960	1975	2000	2025
USA	46	63.2	90.1	114.0
WEC	31	37.5	60.6	78.1
PAC	4	19.4	30.3	40.0
USSR	18	56.4	82.6	101.1
CHINA	21	18.5	49.5	101.4
ROW	8	28.4	98.6	249.8
TOTAL	128	223.5	411.7	684.4

SOURCE: IEA

Table IV. United States market energy use by sector

ENERGY USE: 1960 (QUADS)

USA	OIL	GAS	COAL	OTHER	TOTAL
UTILITY	0.40	1.80	4.69	3.50	10.39
HOUSEHOLD	3.50	5.70	1.08		10.28
INDUSTRY	3.50	5.70	4.90		14.10
TRANSPORT	11.57	0.00	0.00		11.57
TOTAL	18.96	13.19	10.67	3.50	46.34

ENERGY USE: 1975 (EXAJOULES)

USA	OIL	GAS	COAL	OTHER	TOTAL
UTILITY	4.04	3.89	11.08	5.97	24.98
HOUSEHOLD	6.02	9.48	0.22	0.00	15.72
INDUSTRY	3.77	7.84	2.48	0.00	14.09
TRANSPORT	11.89	0.00	0.00	0.00	11.89
TOTAL	25.72	21.21	13.78	5.97	66.68 OR 63.34 QUADS

Table IV. United States market energy use by sector (continued)

ENERGY USE: 2000 (EXAJOULES)

USA	OIL	GAS	COAL	OTHER	TOTAL
UTILITY	2.06	3.60	31.24	13.46	50.36
HOUSEHOLD	7.08	7.61	0.22	0.00	14.91
INDUSTRY	6.12	2.81	3.25	0.00	12.18
TRANSPORT	17.52	0.00	0.00	0.00	17.52
TOTAL	32.78	14.02	34.71	13.46	94.97

ENERGY USE: 2025 (EXAJOULES)

USA	OIL	GAS	COAL	OTHER	TOTAL
UTILITY	5.84	10.73	27.58	24.93	69.08
HOUSEHOLD	7.21	10.51	0.22	0.00	17.94
INDUSTRY	5.54	3.12	4.24	0.00	12.90
TRANSPORT	20.52	0.00	0.00	0.00	20.52
TOTAL	39.11	24.36	32.04	24.93	120.44

fuel type and source sector. Table V presents two scenarios for global non-market energy use.

Discussion of emission factors and projected global emission trends for CO were a part of Dr. Kavanaugh's presentation but will not be summarized here. The assumed N_2O emission factors are presented in Table VI. By combining the energy use trends with these emission factors, the global N_2O emission rates were calculated. Table VII shows the projected emission rates by region and by year while Fig. 8 presents global emission rates graphically. Figs. 9 and 10 present the results in a different format. Fig. 9 presents bar charts segregating N_2O emissions by sector and year, and shows that utilities are the most significant sector. Fig. 10 segregates total projected N_2O emissions by region and shows that the USA is currently the most significant emitter but that the ROW region will dominate in the out years.

Dr. Kavanaugh concluded his remarks with a short list of N_2O research recommendations. He suggested that studies and measurement of NO_x and N_2O from utilities should be conducted with a goal of developing reliable emission factors. He also suggested research to improve estimates of N_2O emission from biomass burning and from mobile sources.

Following Dr. Kavanaugh's presentation there was significant discussion of the results. Dr. Ray Weiss (Scripps Institution of Oceanography) and Dr. Steve Wofsy (Harvard University) suggested that the total emission rate projections were high by approximately a factor of two. The discrepancy was resolved when it was noticed that Dr. Kavanaugh expressed his estimation in terms of N_2O as N_2O, while Drs. Weiss and Wofsy thought the results were expressed as N_2O as N. It was concluded that Dr. Kavanaugh's results were not too high and were in the range estimated by Dr. Wofsy. They also suggested that the transportation emission factor was significantly in error. While that is certainly possible, transportation contributes a relatively small amount to the total projected N_2O emissions from combustion (see Fig. 9).

Dr. Kavanaugh recommended that additional research is required to better quantify N_2O emission factors. Dr. Kavanaugh stressed that his results were preliminary and that constructive criticism of the study would be appreciated.

Table V. Global non-market energy use

(QUADRILLION BTU)

	1960	1975	2000	2025
SCENARIO A	10.7	31.6	25.2	20.4
SCENARIO B	10.7	31.6	20.1	13.0

SOURCE: KAVANAUGH

Table VI. Global N_2O emission factors by sector and source

(LBS/MBTU)

	UTILITIES	INDUSTRY	HOUSEHOLD	TRANSPORTATION
COAL	.23	.05	.03	.03
OIL	.13	.09	.03	.03
GAS	.11	.03	.03	.03

NOTES: COEFFICIENTS CONSTRUCTED BY APPLYING A FACTOR OF 25% TO NOX FACTORS REPORTED BY EPA EXCEPT FOR THE INDUSTRY/COAL CELL AND THE TRANSPORTATION CELLS. INDUSTRY/COAL FACTOR WAS ESTIMATED BY APPLYING A FACTOR OF 12.5% TO THE NOX COEFFICIENT (ABOUT 50% OF THE COAL USED IN INDUSTRY IS USED TO MAKE COKE AND PRODUCES VIRTUALLY NO NOX). A FACTOR OF 3% WAS USED TO ESTIMATE THE FACTORS FOR TRANSPORTATION.

Table VII. Global N_2O combustion emission rates by region and year

(BILLIONS OF POUNDS)

	1960	1975	2000	2025
USA	2.72	4.77	9.12	9.71
WEC	2.27	2.81	4.70	5.26
PAC	0.39	1.53	2.69	3.26
USSR	2.43	4.57	6.02	6.51
CHINA	0.38	1.08	3.00	5.83
ROW	0.94	2.02	5.70	17.27
TOTAL	9.12	16.79	31.23	47.84

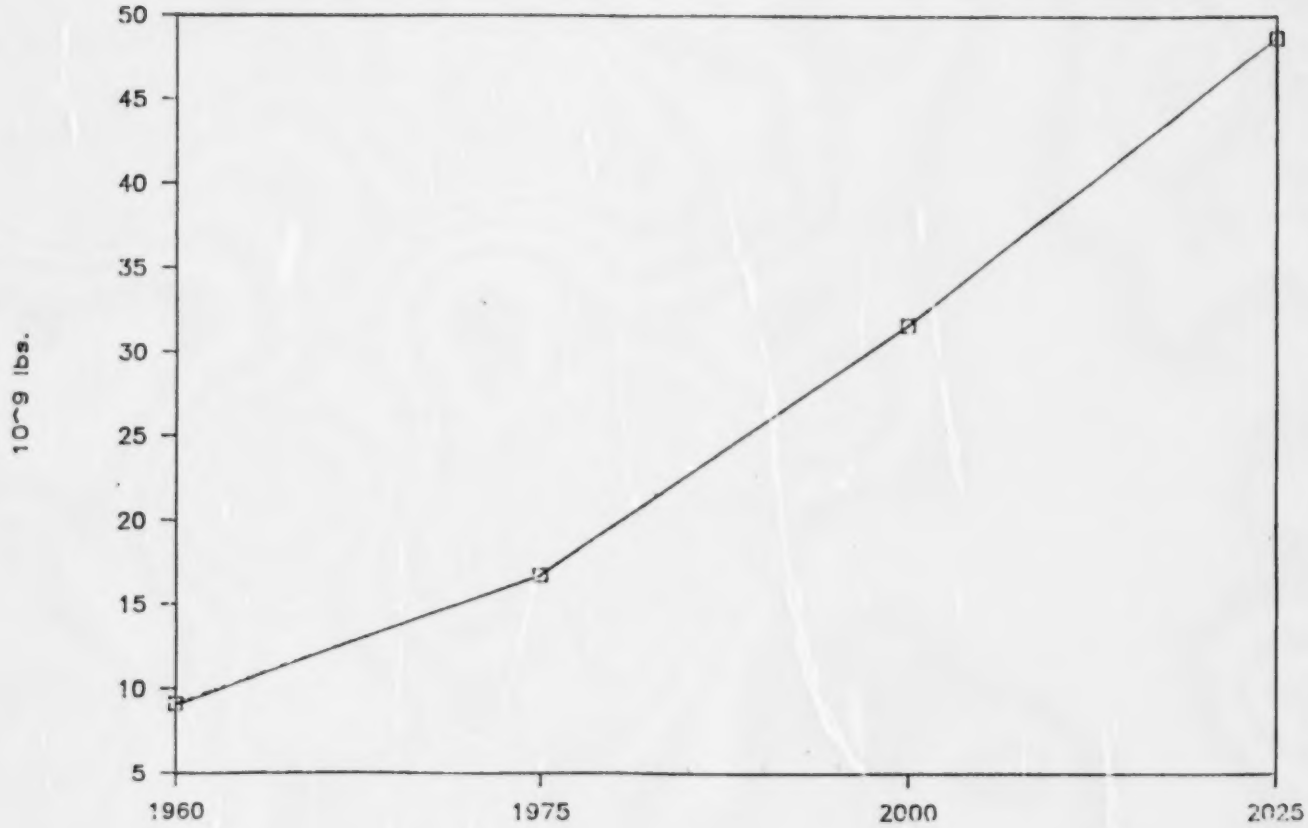


Figure 8. Global N_2O emission rates by year

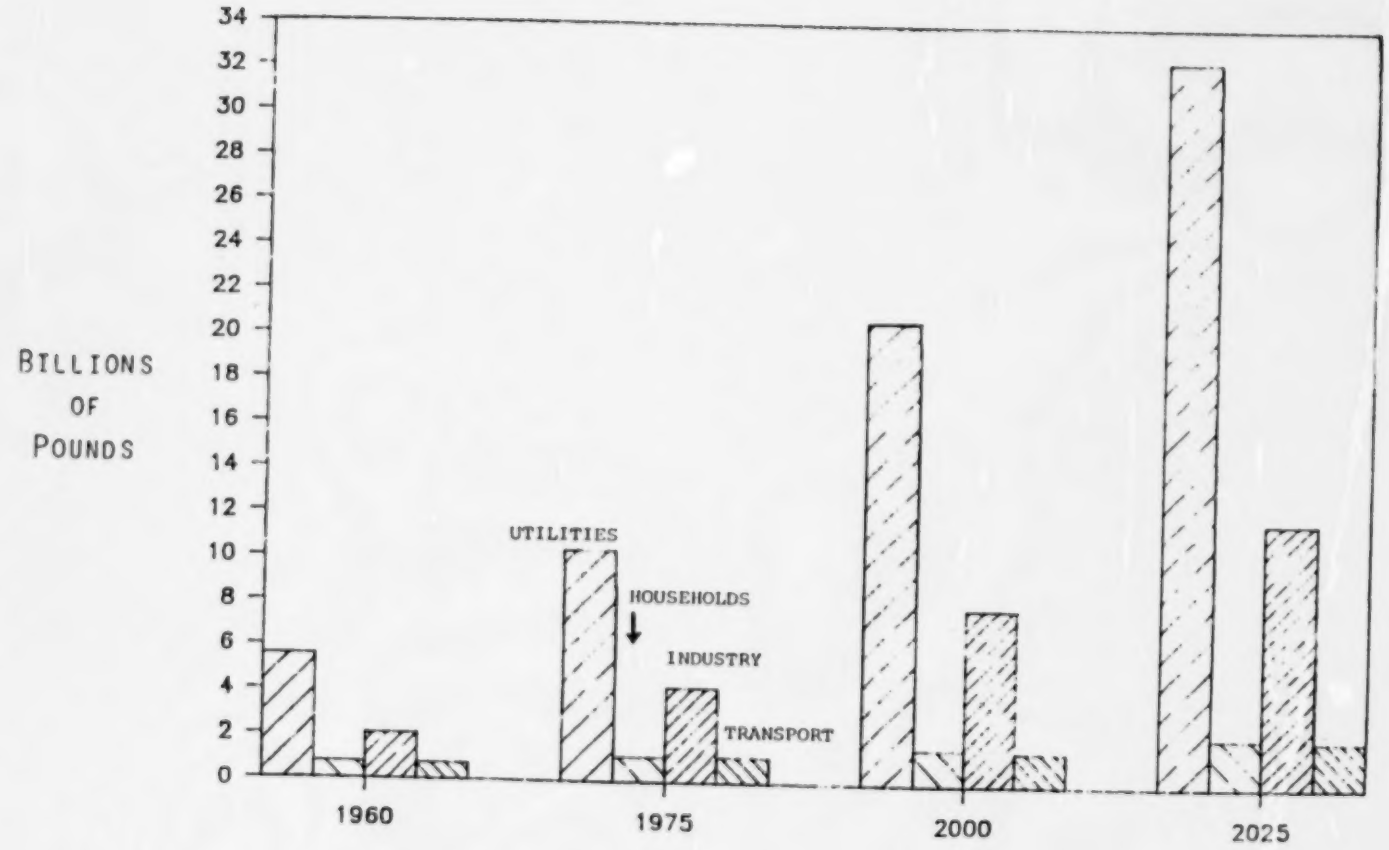


Figure 9. Global N_2O emission rates by sector and year

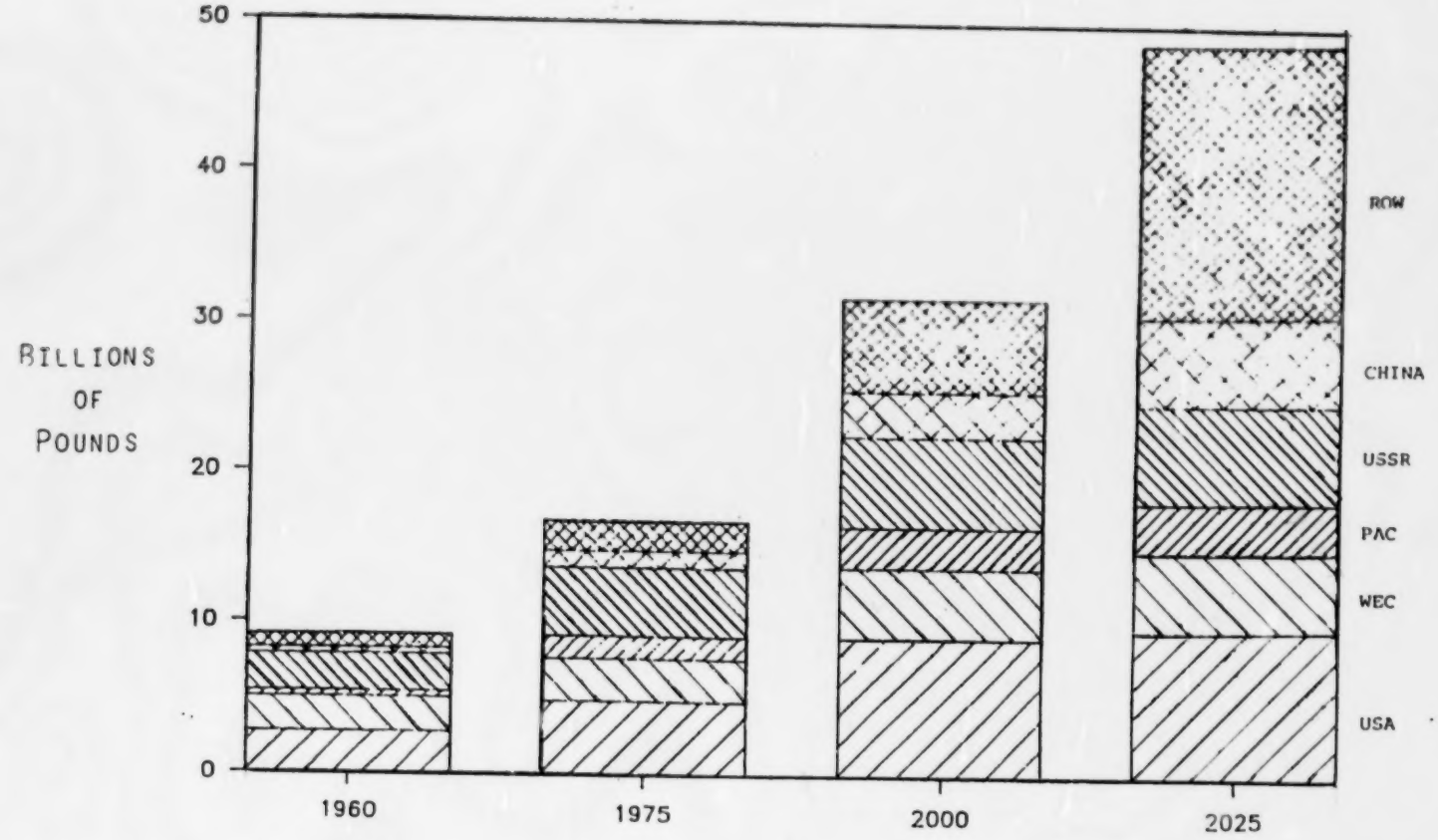


Figure 10. Global N_2O emissions by region and year

TECHNICAL SESSION I--N_2O MEASUREMENTS

One of the obvious concerns in any environmental measurement program is the quality of resultant measurements. Examination of the literature reveals that several measurement techniques have been employed and that for any given technique, variants on the approach are common. This session of the workshop provided a forum to discuss the various measurement approaches, to highlight potential problem areas and to address the steps used in circumventing those problems. Dr. Ray Weiss from Scripps Institution of Oceanography was the discussion leader for this part of the session. Dr. Weiss has been actively involved in atmospheric N_2O measurement and provided some of the first field data on N_2O emissions from utility boilers.[13]

Dr. Weiss' presentation began with a brief review of atmospheric N_2O data showing that the ambient concentration was slightly higher in the Northern hemisphere than in the Southern hemisphere. Data were also presented to show that over the past nine years the ambient concentration of N_2O has increased at approximately 0.55 ppb per year. Next, he presented estimates of the N_2O global fluxes. The total natural flux was estimated to be approximately 0.3 Tmol/year* which is derived from stratospheric removal models assuming no other major sinks. This natural flux is composed of emissions from oceans and terrestrial sources. The flux from oceans was estimated to be approximately 0.1 Tmol/year based on mean oceanic supersaturation of 4 percent and radon-calibrated exchange models. The terrestrial emission flux was estimated to be approximately 0.2 Tmol/year and was calculated by difference including soil sources and sinks. The total anthropogenic flux was estimated to be approximately 0.14 Tmol/year, based on the observed rate of atmospheric N_2O increase and box model calculations. Thus, the total flux is approximately 0.44 Tmol/year with anthropogenic fluxes representing approximately one third of that total. Fig. 11 illustrates this distribution in bar chart format.

Dr. Weiss then presented schematic diagrams of two N_2O measurement systems he has been employing. Both systems are designed to provide absolute concentrations and concentration ratio measurements. The first technique is a gas chromatographic approach using an electron capture detector (ECD) for N_2O measurement and a flame ionization detector (FID) for CO_2 and CH_4 measurement. This technique is illustrated in Fig. 12 and a typical chromatogram is shown

*1 Tmol = 10^{12} gm moles

TOTAL NATURAL: ≈ 0.3 Tmol/yr (from stratospheric removal models assuming no other sinks)

OCEANS: ≈ 0.1 Tmol/yr (from mean oceanic supersaturation of ≤4% and radon calibrated exchange models)

TERRESTRIAL: ≈ 0.2 Tmol/yr (by difference, includes soil sources and sinks)

ANTHROPOGENIC: ≈ 0.14 Tmol/yr (from observed rate of increase and box model calculations)

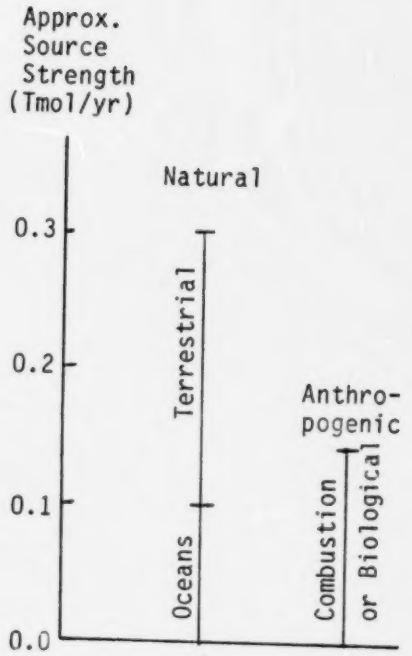


Figure 11. N_2O Global Fluxes

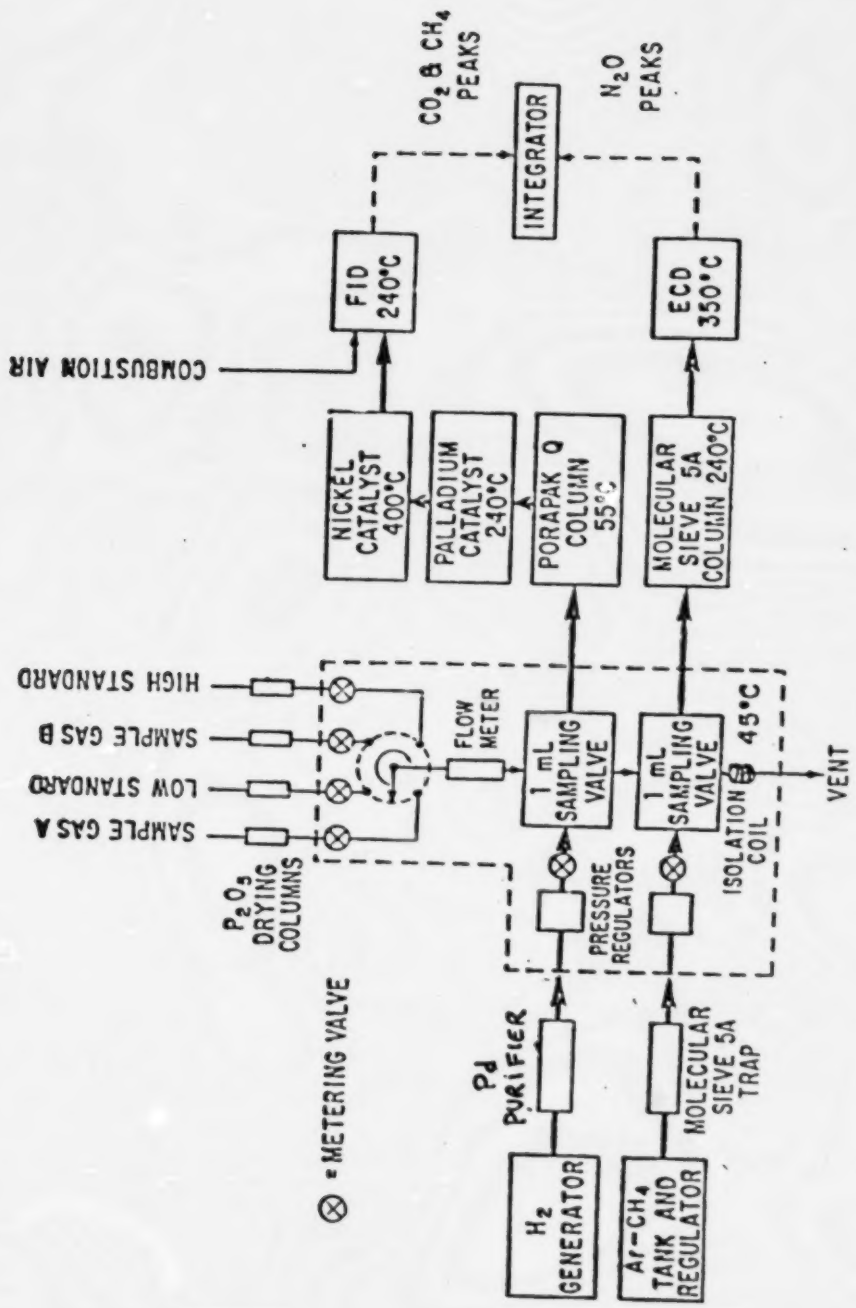


Figure 12. Schematic of N_2O measurement technique using gas chromatography

in Fig. 13. The ECD leg uses AR-CH_4 as the carrier gas. The carrier gas is precleaned with a molecular sieve 5A trap to remove higher hydrocarbons and other potential interfering gases (such as CFCs) from the flow. The actual sample is dried in a P_2O_5 column and stored in a 1 ml sampling loop. N_2O separation is accomplished with a molecular sieve 5A column operated at 240°C.

The second approach used by Dr. Weiss is illustrated in Fig. 14 and employs an ultrasonic detector. A typical recorder trace is shown in Fig. 15. As shown, N_2O separation is achieved with a molecular sieve 5A column.

There was significant discussion of the ECD technique since this approach is widely used in studies performed by other researchers. A variety of important issues were raised and are discussed below.

A. Carrier Gas: A strong preference was expressed for using AR/CH_4 as the carrier gas as opposed to N_2. There is apparently an influence of carrier gas composition on the stability of the ECD detector. Long term variation of detector sensitivity has been observed using N_2 as the carrier gas.

B. Separation Column: Dr. Weiss and Dr. Wofsy prefer to use molecular sieve 5A columns for separating N_2O from other gas species, especially CO_2. Other column types may be utilized but the researcher is urged to prove to himself that there are no interferences and that clean peaks are produced.

C. Column Temperature and Flow Conditions: Low concentration halocarbons have a strong ECD response and often elute from the column at the same time as N_2O. Such halocarbons are often used to clean flasks or gas cylinders. The column temperature and flow conditions should be varied to assure that there are no inadvertent interferences. An additional safety feature is the use of a backflushed precolumn discussed in item D below.

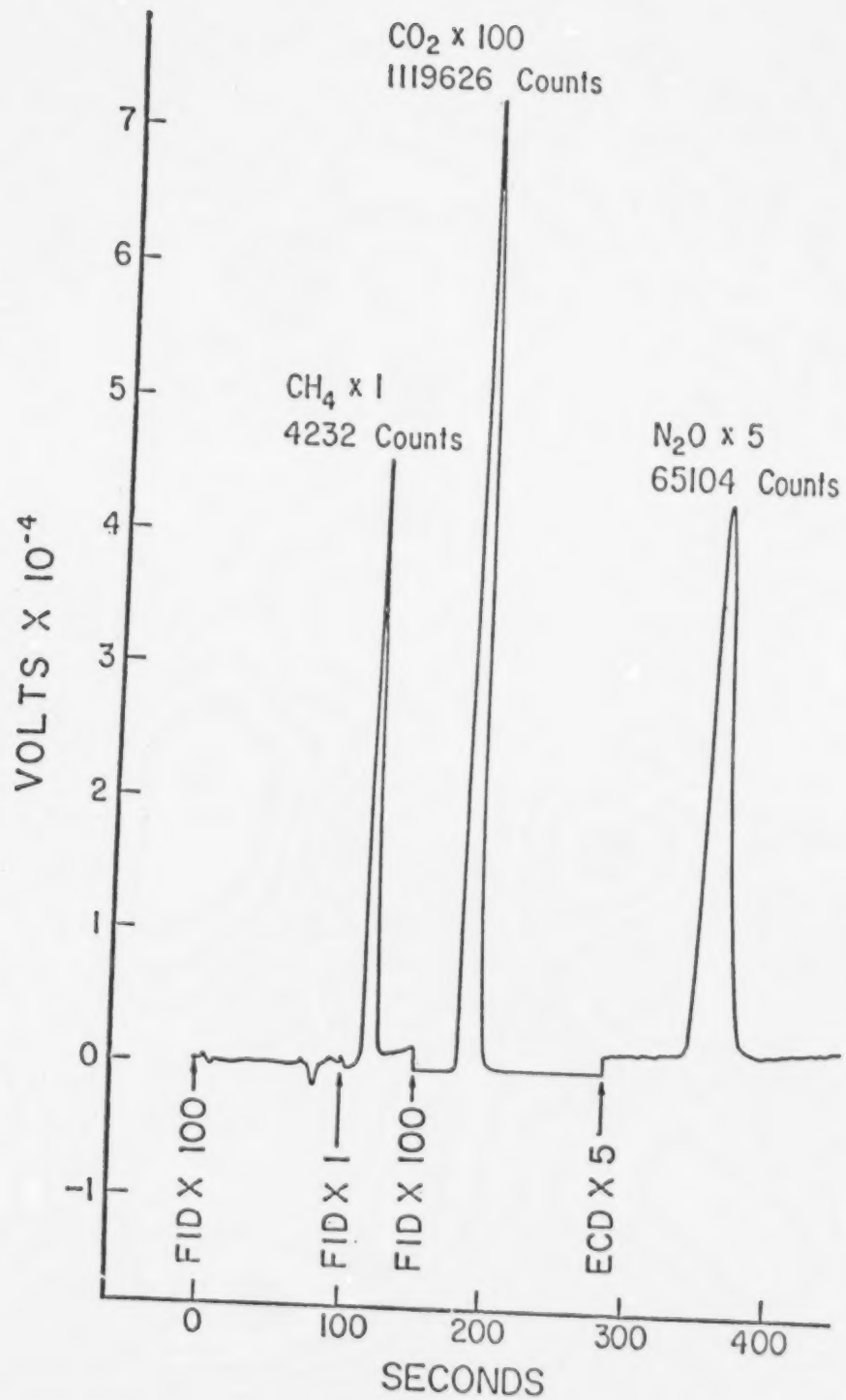


Figure 13. Typical chromatogram

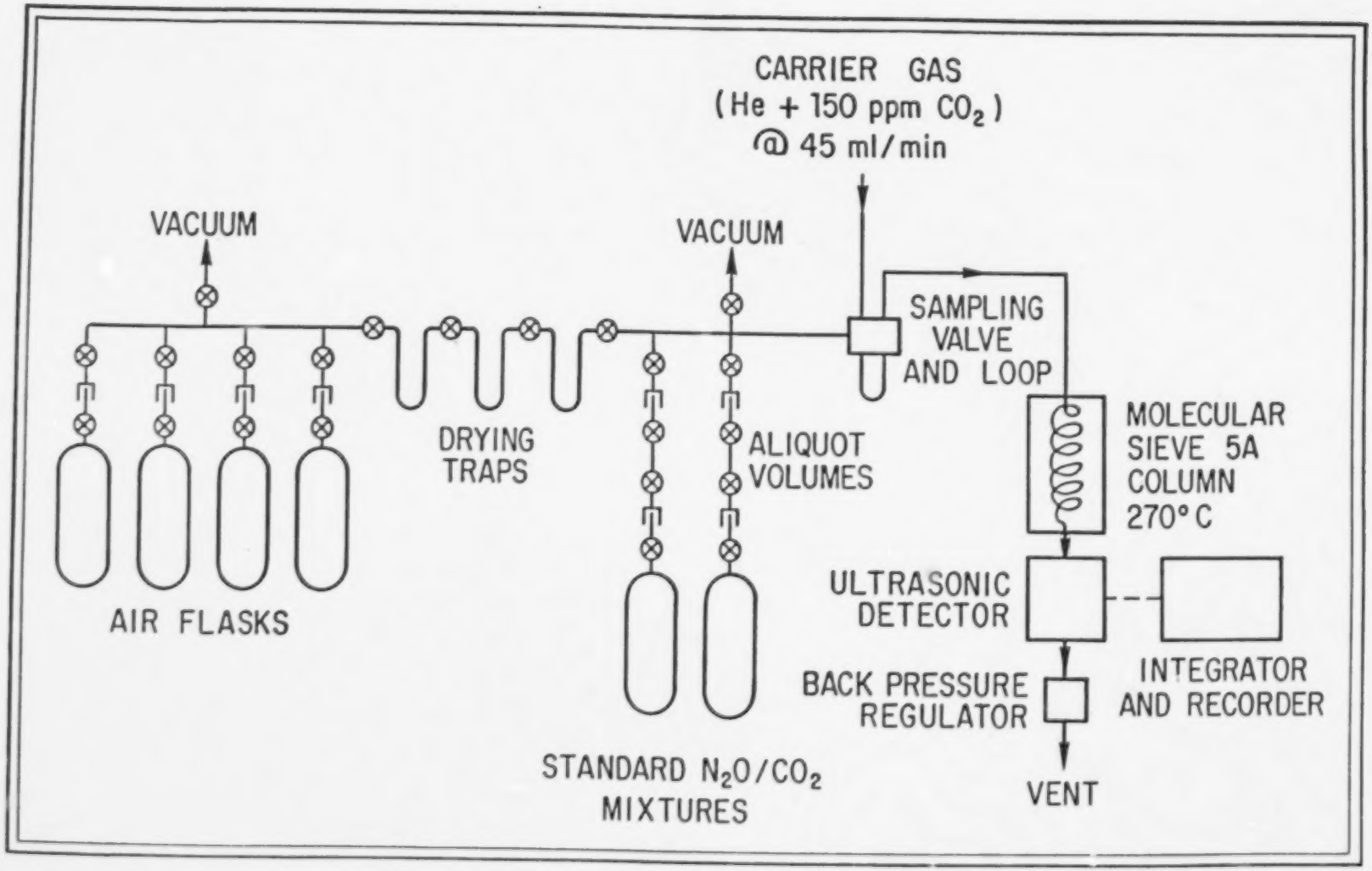


Figure 14. Schematic of N_2O measurement technique using ultrasonic detector

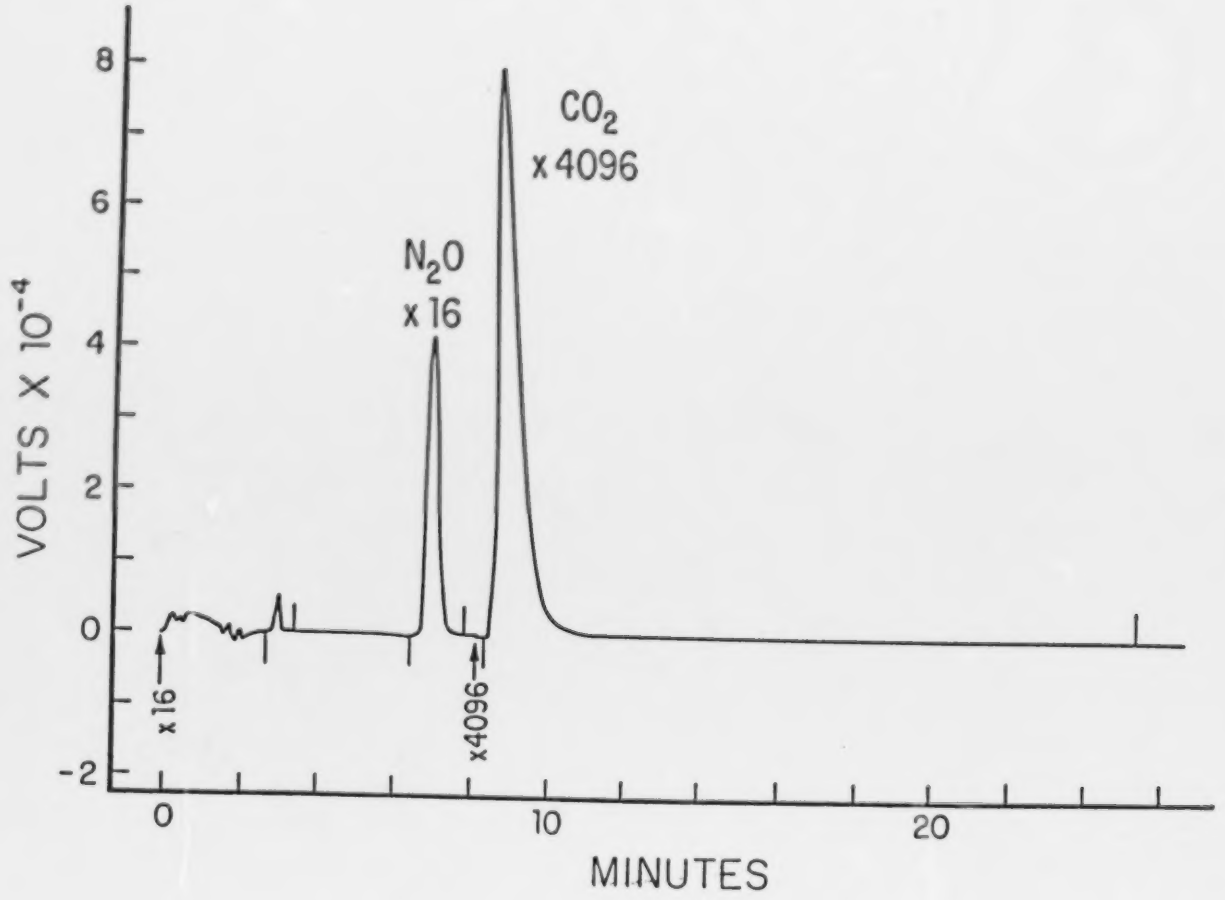


Figure 15. Typical recorder trace from ultrasonic detector

D. Backflush Column: Several species found in combustion exhausts may be trapped on molecular sieve columns and elute over a long time period. This process will cause an upset in the baseline and may contaminate the detector. Dr. Wofsy employs either a Porasil C or Porapak Q precolumn with backflush to protect the molecular sieve column and the ECD detector. This precolumn, operated at about 70°C, will hold up hydrocarbons for several minutes and can be backflushed to remove those species from the system.

E. Sample Drying: Sample gases should be dried prior to the analysis. Various investigators have used a cold trap, a P_2O_5 "Aquasorb" trap or a magnesium perchlorate trap. In extreme cases, chemical cleanup of the sample should be considered. The drying trap should be located at the outlet of the sample flask prior to the sampling valve.

F. Multicalibration: ECD detector output is a nonlinear function of concentration. This nonlinearity should be calibrated over the concentration range of the detector and an empirical formulation developed to represent the effect.

G. Calibration Gas Composition: Calibration gases should be prepared with background gas composition similar to that expected in the sample gas. Generally, the background gas should consist of a mixture of N_2, CO_2, and O_2. Standards of N_2O in pure N_2 should be avoided since the background gases influence detector sensitivity as well as column separation.

H. Sample Loop Conditions: It is important to know the temperature and pressure in the sample loop to precision significantly greater than the required precision of the measurement.

I. Detector: It is assumed that the detector will be a ^{63}Ni constant current cell. For high N_2O samples the ECD should be derated by reducing the standing current and temperature of the detector.

J. Sample Flasks: Either glass or stainless steel sampling flasks have been found satisfactory. Several researchers strongly urged that Tedlar bags be avoided since leakage is commonly observed.

Following the input from attendees, Dr. Weiss prepared a schematic of an ECD set up incorporating the various features addressed. That set up is illustrated in Fig. 16. With extreme care on the part of the researcher, he estimates that the following system characteristics may be expected:

(1)	Precision	0.3%
(2)	Sample Frequency	5 minutes
(3)	Accuracy (systematic error only)	0.1%
(4)	Detection limit	low ppb range

The probable cost for establishing such a measurement system will be in the range of $10K-20K.

As a final note to the ECD measurement technique, Dr. Weiss strongly argued against doing science by consensus. Every experiment will have unique features which must be accounted for. Each researcher is urged to satisfy himself that his work is correct, rather than relying on agreement with others.

Following Dr. Weiss' presentation and discussions, the session addressed N_2O measurement using infrared techniques. A detailed discussion was presented by Dr. James Elkins of NOAA. He addressed N_2O measurement using tunable diode lasers (TDL), fourier transform infrared analyzers (FTIR), and non-dispersive infrared (NDIR) spectrometers.

At the conclusion of his presentation there was considerable discussion of the advantages and disadvantages of each approach. Dr. Elkins and Dr. Mark Zahniser (Aerodyne Research) agreed to prepare a report describing the operation and characteristics of each of these three IR-based techniques. This report is included as Appendix C.

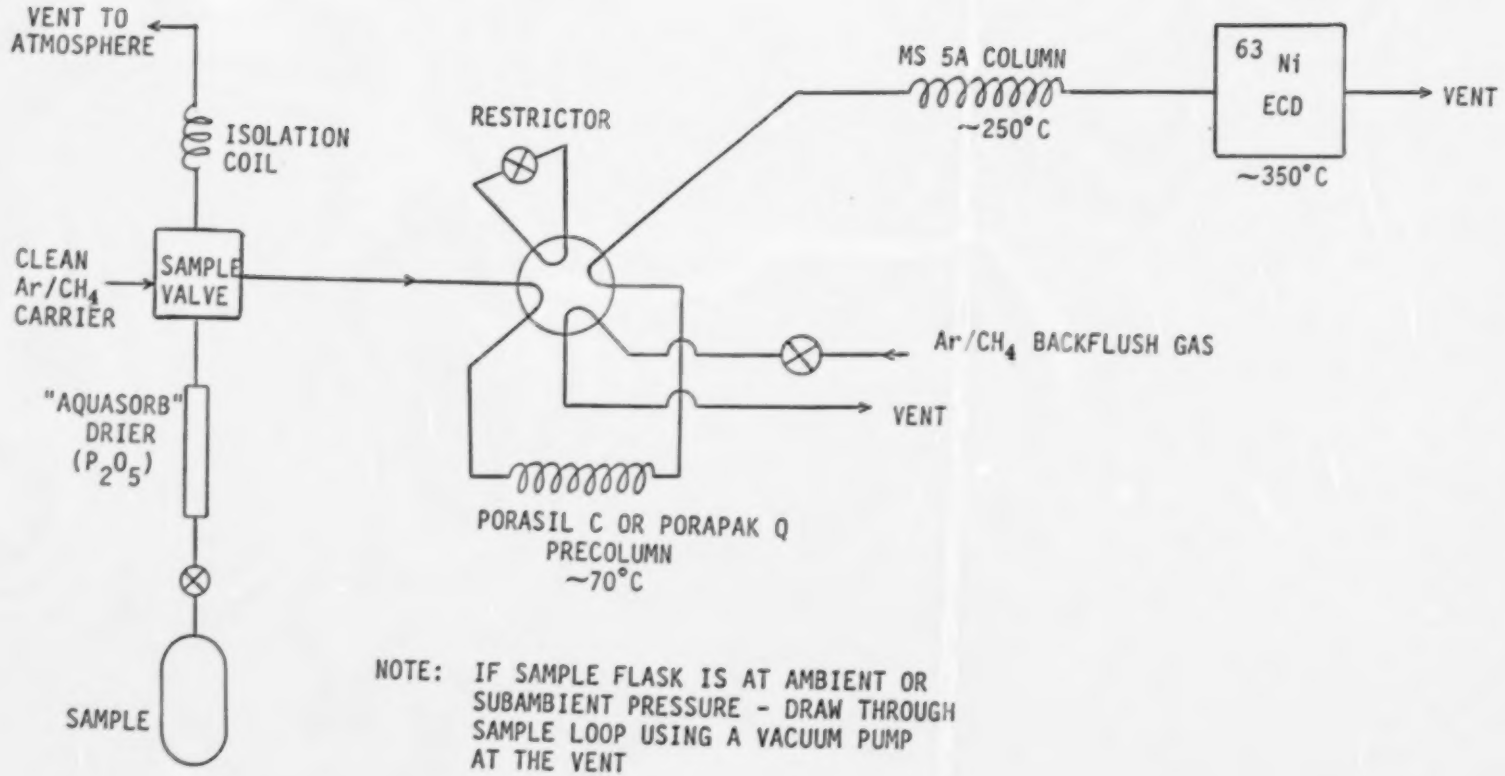


Figure 16. Example GC/ECD schematic for N_2O measurement

At the conclusion of the session there was a general discussion of what technique EPA should employ for combustion research measurements of N_2O. The basic answer reflected Dr. Weiss' warning against science by consensus. The required measurement system is largely dictated by the details of the experiment to be performed. Consideration must be given to the expected N_2O concentration levels, the required measurement precision, the required data turnaround, etc. Table VIII was compiled to illustrate the type of measurement system which could be utilized for various types of experiments. As shown, the ECD approach should be satisfactory for most exhaust gas measurements. It was pointed out that the Electric Power Research Institute (EPRI) is considering a proposal, an element of which includes developing a continuous analyzer to measure N_2O from combustion sources. NDIR is a likely starting point for this work. Based on the input from Dr. Elkins and Zahniser, however, a lower detection limit of 5 ppm is the current state of the art for NDIR (see Appendix C).

As a final note to the discussion in this session, Dr. Elkins informed the participants that the National Bureau of Standards is now offering N_2O standard gas mixtures suitable for atmospheric measurement calibrations. Data sheets for these NBS standards and ordering information were made available. It is noted that standards with N_2O and CO_2 concentrations commensurate with boiler exhaust speciation are not available. Dr. Elkins also suggested that commercial instrument manufacturing firms might be of significant benefit in the measurement area and that advanced instrumentation might become available rapidly if EPA could identify the requirements.

Table VIII. Comparison of measurement systems for various applications

Measurements	Standards	Chromatography		FTIR	DIODE IR	NDIR
		ECD	N_2O/CO_2			
Ambient	X*	X	X			
Stack		X				X
Plumes		X	X	X	X	X
Flame					X	

*Standards available only for ambient measurements. Standards are needed for all measurements.

TECHNICAL SESSION II--N_2O FORMATION MECHANISMS

The second technical session of the workshop examined the understanding of chemical, thermal, and fluid mechanic processes responsible for N_2O formation and destruction in flames. The initial intent was to establish a working hypothesis of the controlling mechanisms which could then be used to propose potential N_2O control mechanisms.

The discussion leader for the initial portion of the second session was Dr. W. Steven Lanier (EER). Dr. Lanier opened the session by presenting N_2O emission data gathered by Acurex Corporation as part of EPA's NO_x Environmental Assessment Program. Those results, shown in Fig. 17, indicate a direct relation between N_2O emissions and NO_x emissions. Included in the data set are results from stack tests conducted on boilers firing coal, coal-oil mixture, coal-water slurries, oil, and refinery gas. There is some scatter in the data but the correlation suggests that the exhaust N_2O concentration is approximately 25 percent of the NO_x exhaust concentration (on a volume basis). The clear implication of these data is that combustion modifications which reduce NO_x emissions will result in an equal fractional reduction in N_2O emissions.

Dr. Lanier noted that recent test results obtained by Dr. Larry Muzio of Fossil Energy Research Corp. in an EPRI sponsored study were consistent with the Acurex results. It was also noted that a recent joint study involving Harvard University, MIT, and Aerodyne Research had examined N_2O and NO_x concentration in a coal-water slurry fired research facility. This latter study also concluded that N_2O and NO_x exhaust emissions were directly related but found a slightly higher N_2O:NO_x ratio than that reported by Acurex.

Next Dr. Lanier presented results from another EPA sponsored study conducted by EER under the FCR II program.[14] In this study, exhaust emissions were measured from a small pilot scale research facility burning coal under staged combustion conditions. The facility is shown schematically in Fig. 18. Combustion air was introduced with the fuel and through downstream staging ports. By diverting combustion air from the primary zone to the secondary ports, it was possible to vary the stoichiometric ratio in the initial burning zone while maintaining a constant excess air level in the boiler exhaust. This is classical staged combustion and is the basis for NO_x reduction in low NO_x coal and oil burners. The particular facility used in these tests was

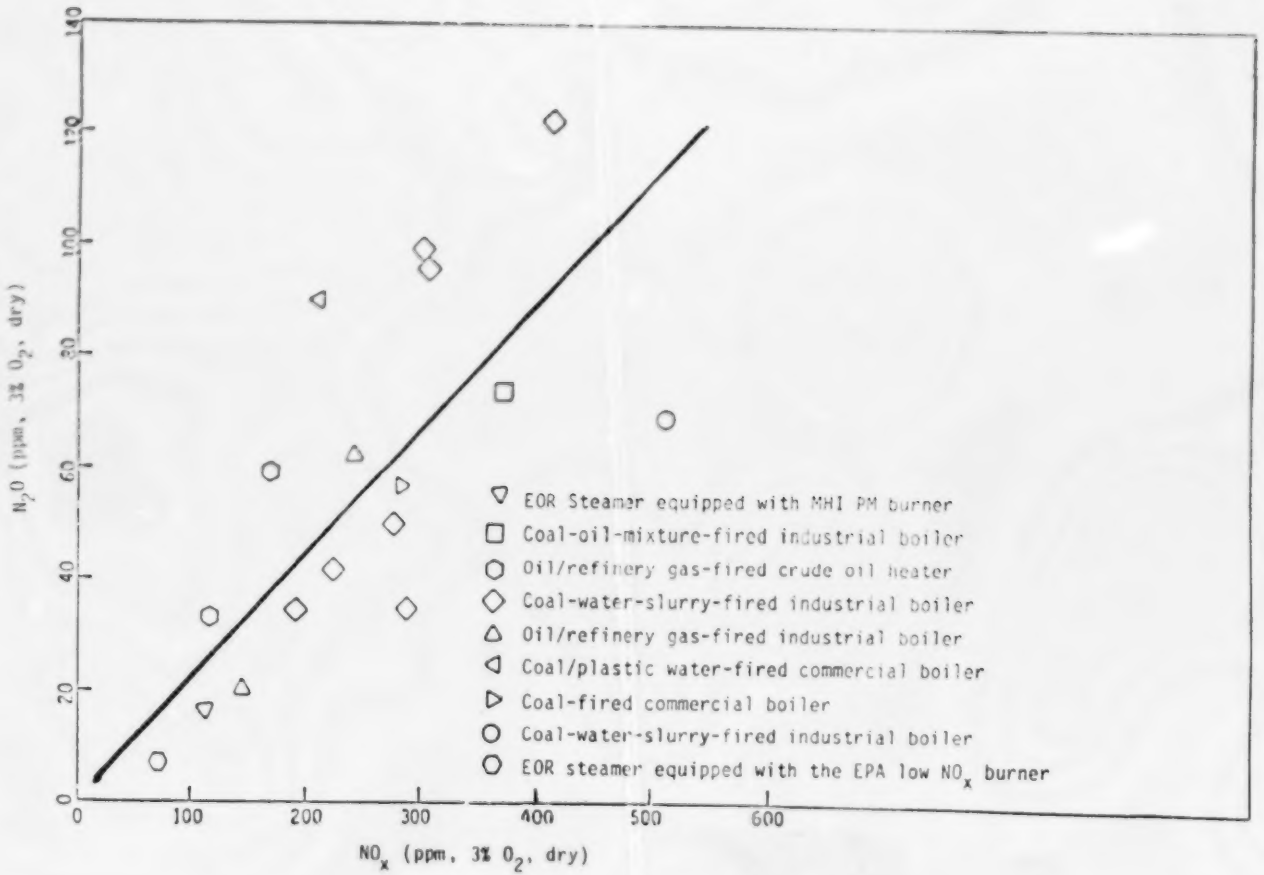


Figure 17. N_2O emission from combustion sources as a function of NO_x emissions
Source: "Environmental Assessment of an Enhanced Oil Recovery Steam Generator Equipped with a Low-NO_x Burner, Volume 1. Technical Results," EPA Report No. 600/7-86-003A, 1986.

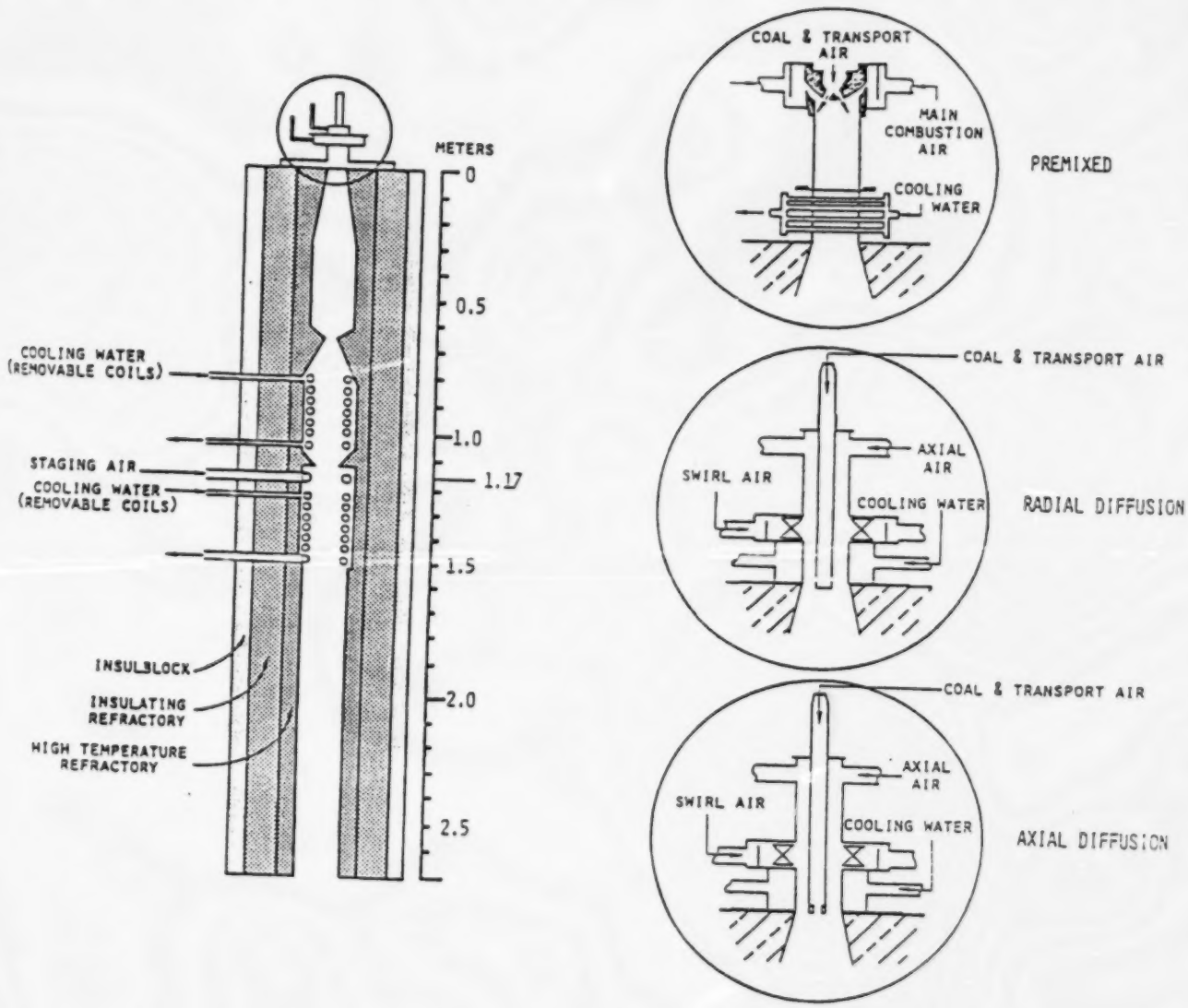


Figure 18. Details of pulverized coal furnace system

equipped with removable cooling coils in the primary combustion chamber which permitted examination of thermal environment effects. Exhaust NO and N_2O emission results are presented in Fig. 19 as a function of primary zone stoichiometric ratio (SR_1). In all tests, the exhaust stoichiometric ratio was held constant at SR_{ex} = 1.3 (30 percent excess air). In the unstaged tests (SR_1 = SR_{ex} = 1.3) the exhaust NO level was approximately 1200 ppm. Under staged conditions, the exhaust NO level fell to about 350 ppm in the uncooled trials and to approximately 200 ppm in the cooled trials. For the uncooled trials, the exhaust N_2O emissions were essentially constant while a slight increase in N_2O emissions was recorded from staging the cooled flames. Thus, reducing NO emissions between 70 and 80 percent resulted in essentially no variation (or even a slight increase) in the N_2O emission rate.

Dr. Lanier pointed out that these different sets of experimental data result in contradictory indicated N_2O emission trends. The field test results indicate that NO_x controls result in proportionately equal N_2O emission reduction. The EER pilot scale tests indicate that NO and N_2O emission rates are unrelated. The participants were then challenged to explain the reason for the apparent discrepancy. If both sets of data are experimentally correct, then the apparent implications of the data sets cannot be globally correct. That is, under certain conditions, the direct correlation must no longer hold.

Dr. Lanier then suggested that it was critically important to understand how N_2O is formed and destroyed in the combustion process. If the controlling processes can be understood, it may be possible to identify the conditions under which an N_2O:NO_x relation holds and devise control approaches to minimize N_2O combustion emissions. It was noted that chemical kinetic modelling of NO_x formation and destruction had been underway for nearly two decades and that relatively sophisticated models were available to describe the controlling processes. One of those chemical models had been developed by EER under DOE and EPA sponsorship and had been widely tested against available NO_x emission results under a variety of combustion conditions. The chemical description for combustion of nitrogen bearing fuels consisted of approximately 180 reactions in 39 species with each reaction occurring simultaneously in both directions. Fig. 20 illustrates the basic steps by which fuel bound nitrogen from coal is processed to form NO or N_2. One pathway for forming molecular nitrogen (N_2) begins with a reaction between amine radicals (NH_i)

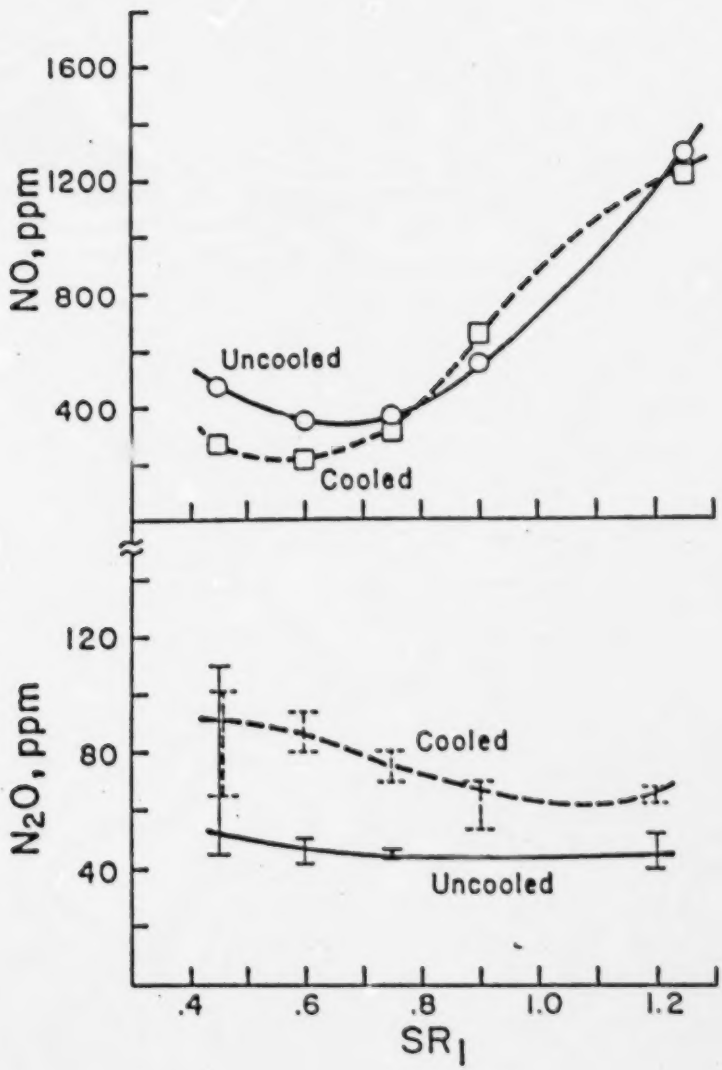


Figure 19. Exhaust NO and N_2O emissions as a function of stoichiometric ratio

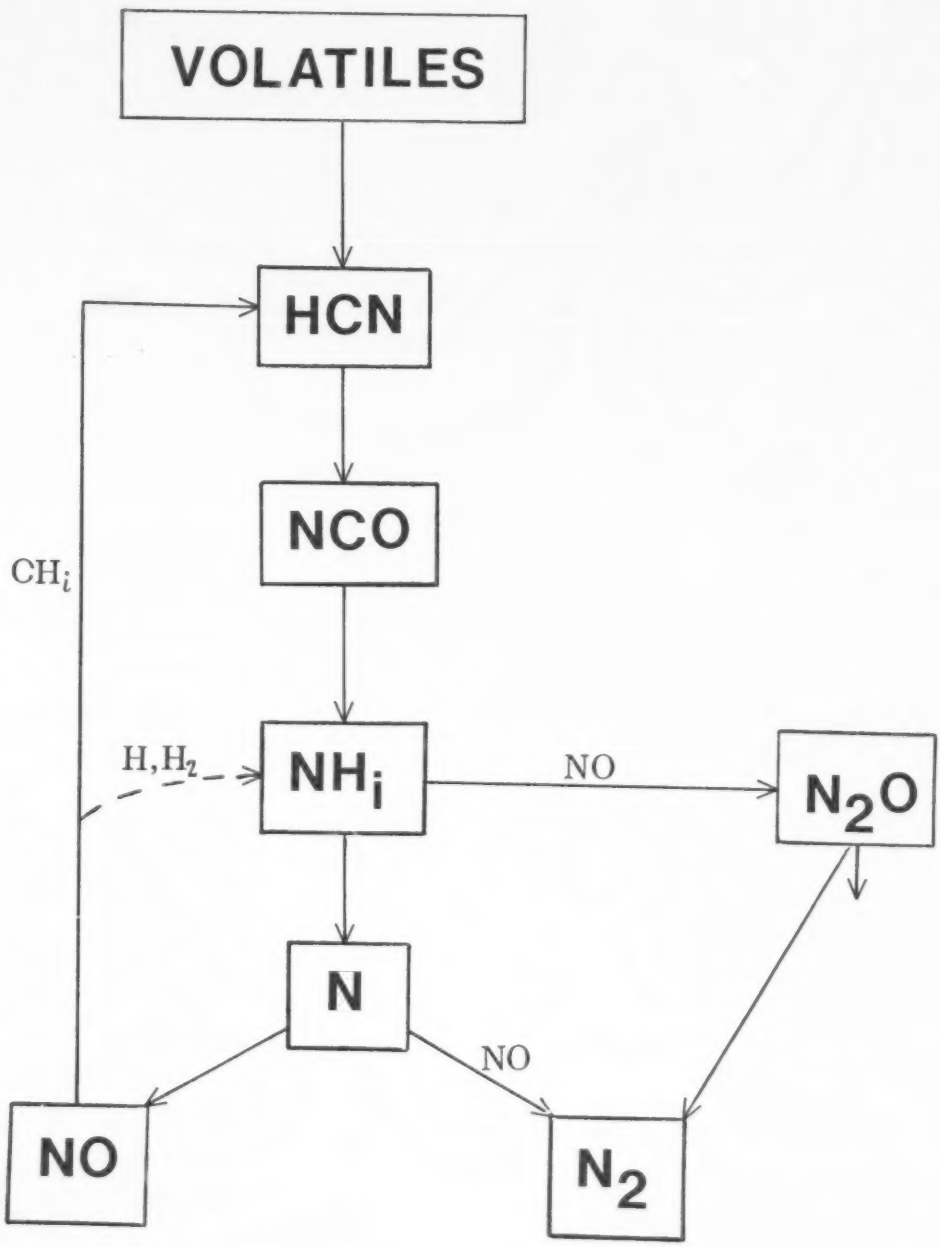


Figure 20. Mechanism for N_2O formation

and the NO molecule to form N_2O. This N_2O can either react with an H atom to form N_2 + OH or it may exit the system. This is the dominant path for formation and destruction of N_2O included in the model. Except under specialized conditions, such as extremely rapid quenching, this model has never predicted ppm level N_2O concentrations in reactor exhausts.

In a recent paper by R. A. Perry,[15] from Sandia National Laboratories, the reaction of NCO with NO was examined and the suggested reaction products were N_2O + CO. Dr. Lanier had speculated that addition of this N_2O formation pathway might bring the predicted N_2O exhaust emissions more in line with the levels observed in field and pilot scale tests. To test that speculation, two sets of calculations were performed in which a high nitrogen fuel was burned in a 25 percent excess air environment. The bound nitrogen was simulated as HCN and the combustion process was simulated as a 5 msec well stirred reactor followed by a 200 msec plug flow reactor. In the first set of calculations, the only mechanism for N_2O formation was that illustrated in Fig. 20. This pathway is referred to as N_2O path I. Fig. 21 presents the calculated NO and N_2O profiles with two different assumed temperature profiles in the plug flow reactor. As shown, the NO concentration is on the order of 900 ppm which is consistent with the measured NO_x levels from lean combustion of 1 percent N fuels.[16] The predicted N_2O emission levels are well below 1 ppm, consistent with previous experience using this model.

A second set of calculations was then performed with the N_2O formation path suggested by Perry (N_2O path II) included in the reaction mechanism. Results from these calculations are presented in Fig. 22. It is noted that the predicted exhaust N_2O concentrations remain well below 1 ppm but that the NO concentrations are markedly depressed. The implication of these results is that N_2O reaction path II is rapid but that any N_2O formed is then converted to N_2. This depletes the pool of reactive nitrogen species and limits the production of NO.

Results from several other simulation attempts were presented including distributed fuel addition (to simulate finite rate fuel volatile release) and staged combustion. In every case, the predicted N_2O concentrations were well below 1 ppm and addition of N_2O reaction path II served to significantly depress the predicted NO concentration.

Dr. Lanier concluded from these simulations that current understanding of processes controlling N_2O chemistry is insufficient. He suggested that the

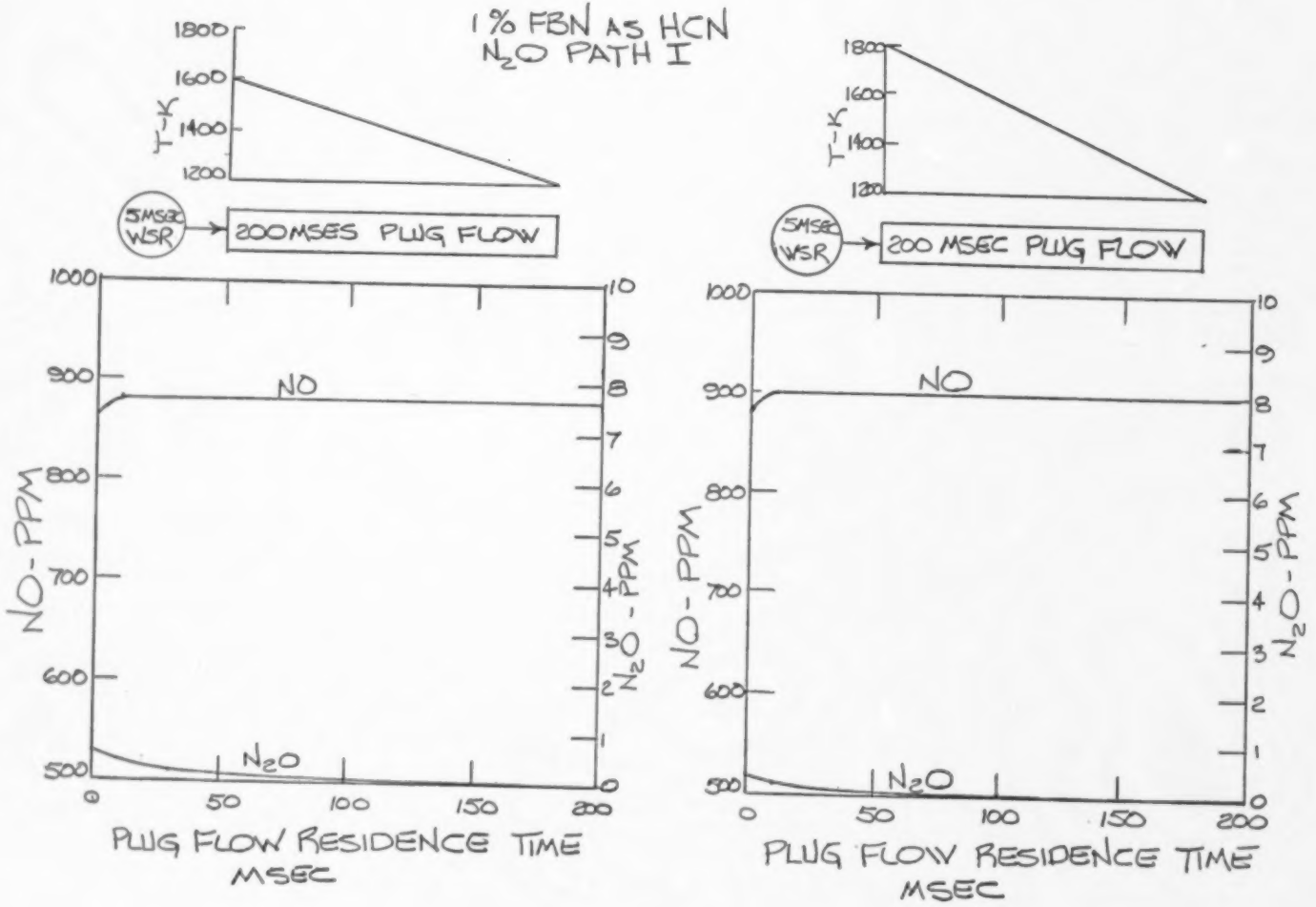


Figure 21. NO and N_2O profiles in a plug flow reactor for two temperature profiles with N_2O formation Path I

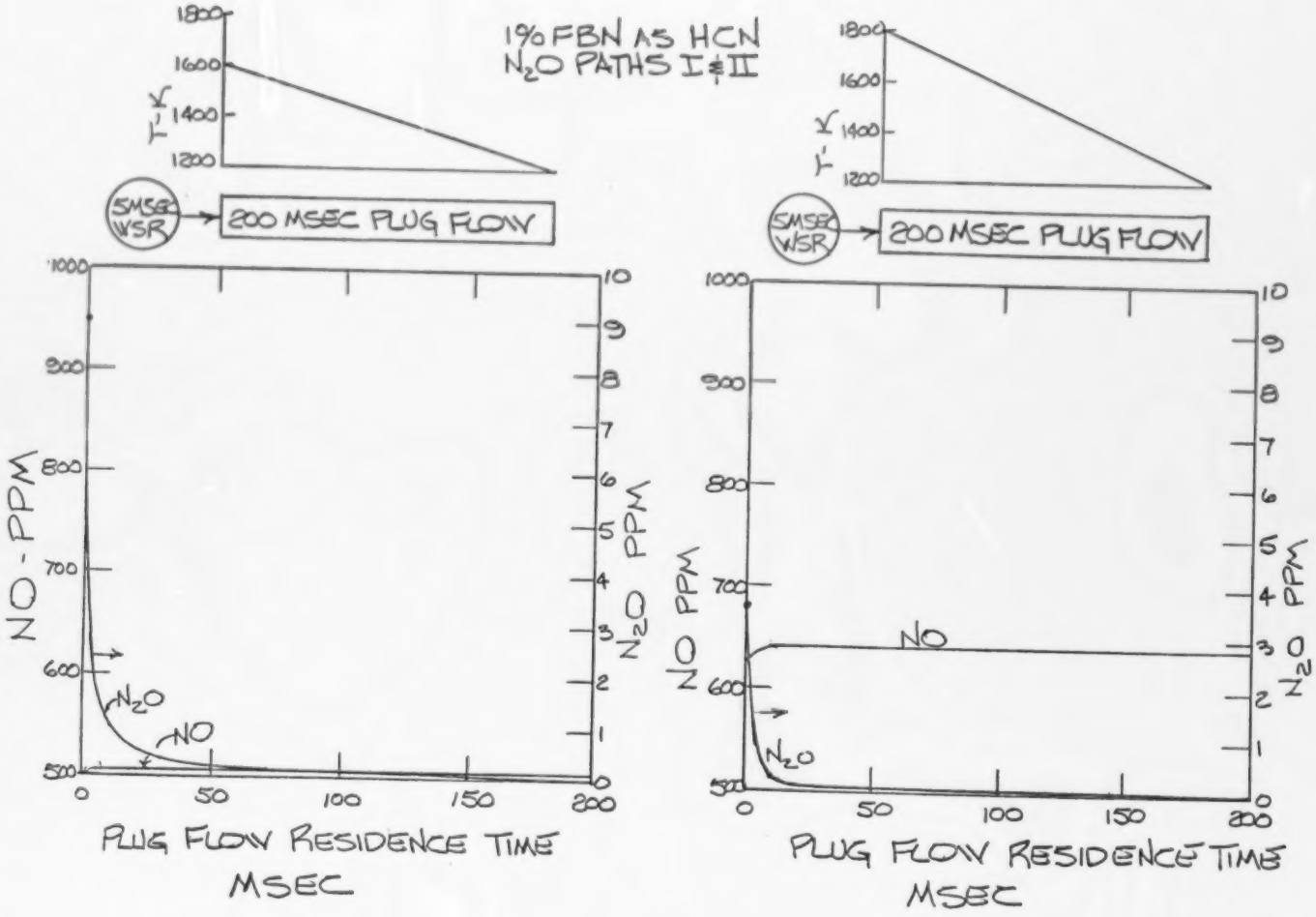


Figure 22. NO and N_2O profiles in a plug flow reactor for two temperature profiles with N_2O formation Paths I and II

reaction paths for N_2O formation and N_2O destruction should be critically examined. He warned, however, against indiscriminate adjustment of reaction rates to force agreement with N_2O emission trends. The existing reaction sets have been carefully developed over the years to predict NO_x, HCN, and NH_i data trends. Addition of new N_2O reaction paths and/or adjustment of reaction rates should be carefully examined to assure that agreement with the NO_x data base is maintained.

Following Dr. Lanier's remarks, Dr. Nancy Brown (Lawrence Berkeley Laboratories) described results from laminar, premixed flat flame experiments. Experiments burning both CH_4/air and H_2/air had been conducted with the reactants doped with either N_2O or NH_3. Centerline axial profiles of CO, CO_2, NO_x, N_2O, and O_2 had been recorded. Little difference in the N_2O profiles were observed between H_2 and CH_4 fuel systems. When N_2O was added to the reactants, it did not survive the flame front. With NH_3 doping, N_2O formation was observed but was destroyed in the active flame. One of the advantages of flat flame burners is that such devices produce radially uniform species concentration profiles. In these experiments, it was found that substantial N_2O concentrations existed on the outer edges of the flame, suggesting that rapid quenching is an important process in allowing N_2O to escape flame zones.

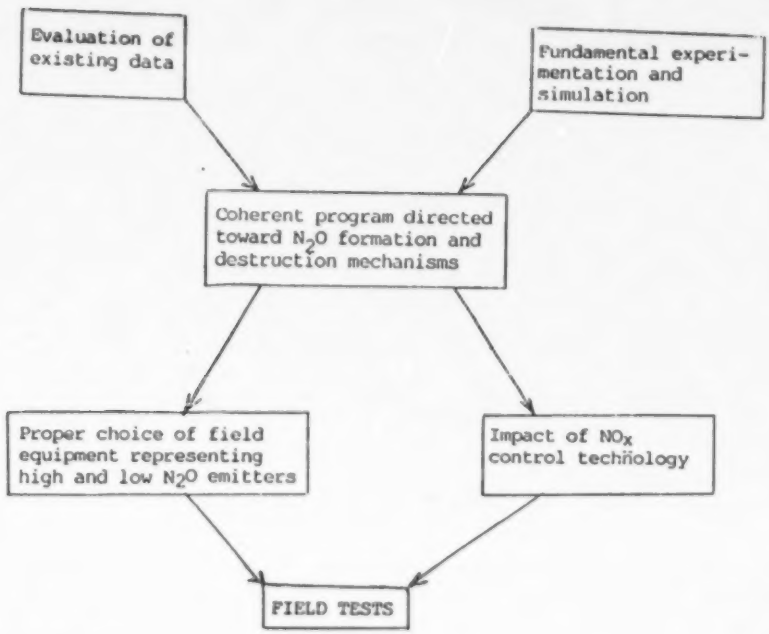
Dr. J. O. L. Wendt (University of Arizona) led the next part of Session II. He presented a set of "strawman" R&D recommendations and a definition of a possible R&D approach. This R&D recommendation began with an assessment of what is currently available. This included:

(1) fragmentary and conflicting measurements of N_2O in pilot furnaces and field units;

(2) isolated benchscale experiments in which
(a) a Nitrogen elemental balance was attempted,
and (b) N_2O was measured;

(3) two decades of data on fuel bound nitrogen conversion and intermediates formed during combustion.

Dr. Wendt concluded that what is needed is a program structured as shown below.


Evaluation of existing data
Fundamental experimentation and simulation
Coherent program directed toward N_2O formation and destruction mechanisms
Proper choice of field equipment representing high and low N_2O emitters
Impact of NO_x control technology
FIELD TESTS

Dr. Wendt continued with a possible R&D approach which consisted of three main elements. The first element that was suggested consisted of numerical simulation studies designed to:

(1) identify N_2O formation pathways;

(2) identify critical data gaps;

(3) establish firm hypotheses for experimental testing.

The second suggested approach elements were laboratory flame studies, with and without coal. These experiments should be designed to:

(1) refute or confirm hypotheses relative to likely pathways for N_2O formation;

(2) establish useful candidates for subsequent field testing. Potentially high and low N_2O emitters should be identified;

(3) suggest N_2O control strategy.

The third element would be a field test program for N_2O emission factor development. In addition to establishing N_2O emission factors this element should also be designed to confirm hypotheses established from the fundamental

work. Dr. Wendt emphasized that, in his opinion, the field test activities should follow the other program elements rather than lead them.

Dr. Wendt's comments represented his honest opinion but were purposefully presented to evoke discussion. To that end, he was certainly successful in that strong agreement and disagreements were expressed. It is the current author's recollection that with few exceptions, the expressed opinions consistently reflected the type of research in which the individual had been involved. Fundamental combustion researchers tended to agree with Dr. Wendt's R&D priorities. Pilot scale combustion researchers generally felt that the laboratory flame studies should have highest priority, while atmospheric scientists emphasized that field data should be given high priority. Clearly there was no consensus opinion from the assembled group.

Following a short break, the session continued with a brief discussion by Dr. John Kramlich of EER, who had performed the experiments discussed earlier by Dr. Lanier. His initial thrust was to clearly explain the design and operation of his experimental facility (Fig. 18). He discussed additional NO and N_2O data obtained while firing natural gas doped with NH_3 to the same nitrogen content as in the coal fired tests. The NO emissions were very similar to those from coal but the N_2O emission levels were below his measurement detection limit (less than 5 ppm). This finding is consistent with results obtained by the Harvard/MIT/Aerodyne group and suggests that there is something different about coal flames relative to N_2O. Dr. Kramlich suggested that surface reactions involving soot, coal char, or coal ash could catalyze N_2O formation. He also pointed out that his coal results with cooling resulted in significantly higher N_2O emission rates (Fig. 19). This finding was consistent with the flat flame observations discussed by Dr. Brown and suggested that the full temperature profile (axial and radial) could be very important in dictating exhaust N_2O emission levels.

Several of the earlier discussors referred to results from pilot scale studies conducted jointly by Harvard University, MIT, and Aerodyne Research. Dr. Wofsy provided an overview of this study which included field testing, pilot scale research, and chemical kinetic modelling. The pilot scale research was performed at MIT's combustion research facility and has been documented in a paper to be included in a poster session at the 21st Symposium (International) on Combustion (August, 1986). A preliminary copy of this paper was provided to the workshop participants. These pilot scale tests

examined combustion of gas, oil, and coal-water slurry under normal and staged conditions. The experiments consisted of exhaust measurements and in-flame measurements taken on the flame centerline.

Fig. 23 shows the centerline concentrations of O_2, CO_2, NO_x, and N_2O from coal-water slurry and heavy oil firing (under unstaged conditions) as a function of axial distance from the furnace front wall. At the top of Fig. 23, the approximate temperature profile in this 1.2m x 1.2m cross-section, 10m long facility (3MW$_t$ heat input) is presented. As shown, the N_2O and NO_x concentration profiles closely follow each other through the combustor. Figs. 24 and 25 present similar data from firing coal-water slurry and natural gas under staged combustion conditions. For coal-water slurry firing, the NO_x and N_2O profiles mirror each other except in the region where secondary air enters the system. Note the sharp rise in N_2O and fall in NO_x near the 2-meter location. For gas firing (staged), the N_2O and NO_x profiles are mirror images throughout the furnace, but note that the N_2O concentration is reported in parts per billion as opposed to ppm levels reported in Figs. 23 and 24.

Dr. Wofsy noted that these gas results compare favorably with those presented by Dr. Kramlich earlier in the session, giving further evidence that fuel type and combustion type are important parameters in defining N_2O emission rate. This also suggests that much of combustion generated N_2O is derived from chemical processes associated with oxidation of fuel bound nitrogen.

The results from the coal-water slurry and oil firing tests discussed above were then presented in a composite form comparing N_2O and NO_x concentrations. The comparison is illustrated in Fig. 26, which shows a linear correlation of the same type found by Acurex (Fig. 17). It should be noted that the correlation has a non-zero intercept and that the slope of the curve is significantly greater than that found by Acurex (35-39 percent vs. 22-25 percent). It is significant that a linear relation was observed for both staged and unstaged trials.

The next portion of Dr. Wofsy's presentation dealt with field test results from utility boilers and biomass fired systems. The thrust of the examination was to determine the relationship of N_2O emissions and the bound nitrogen content of fuel. Fig. 27 presents a correlation from utility boiler field tests firing natural gas, residual oil, and pulverized coal, in which the exhaust N_2O to CO_2 ratio is found to depend on the nitrogen to carbon

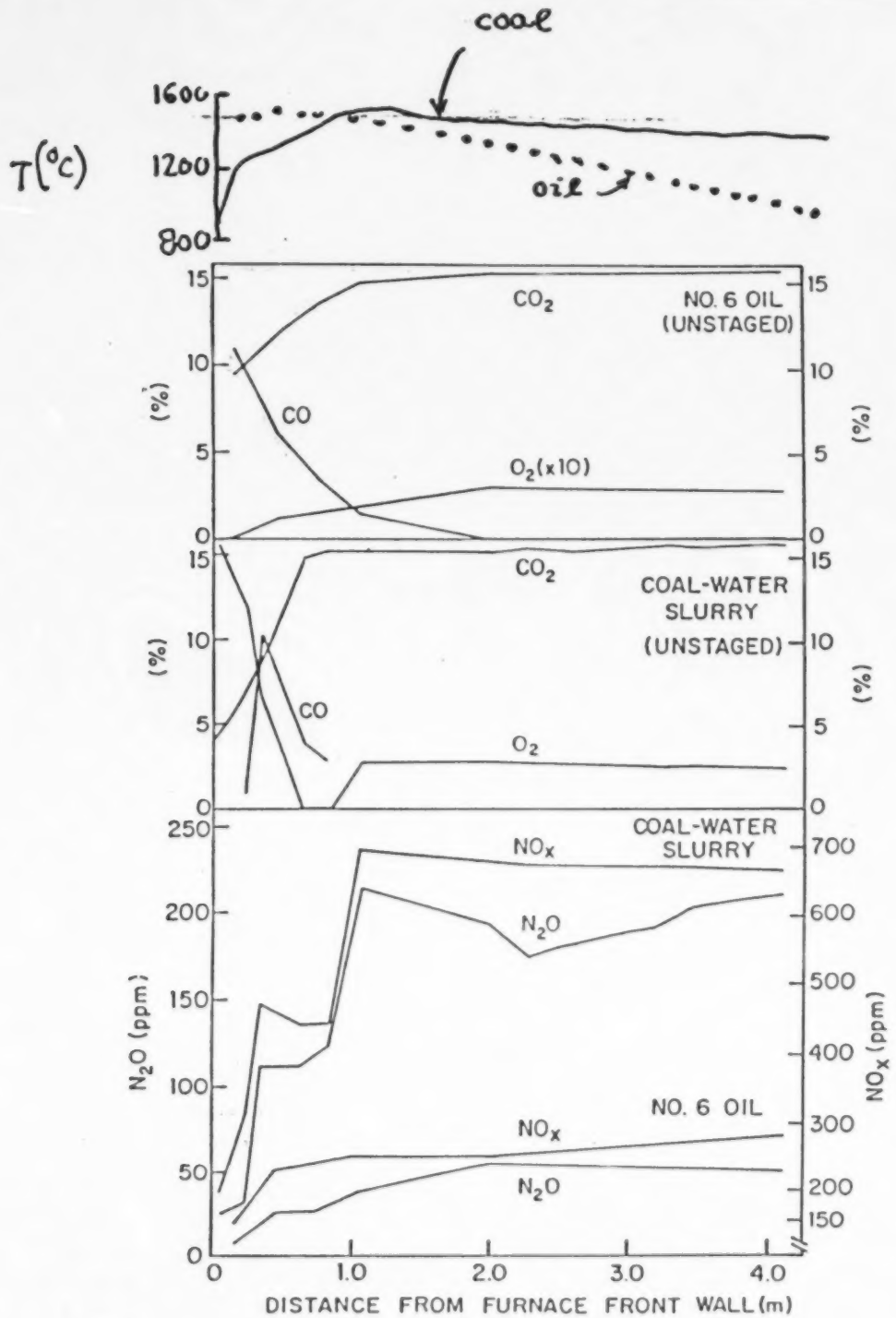


Figure 23. Centerline concentrations of O_2, CO_2, NO_x, and N_2O in MIT combustion facility under unstaged conditions

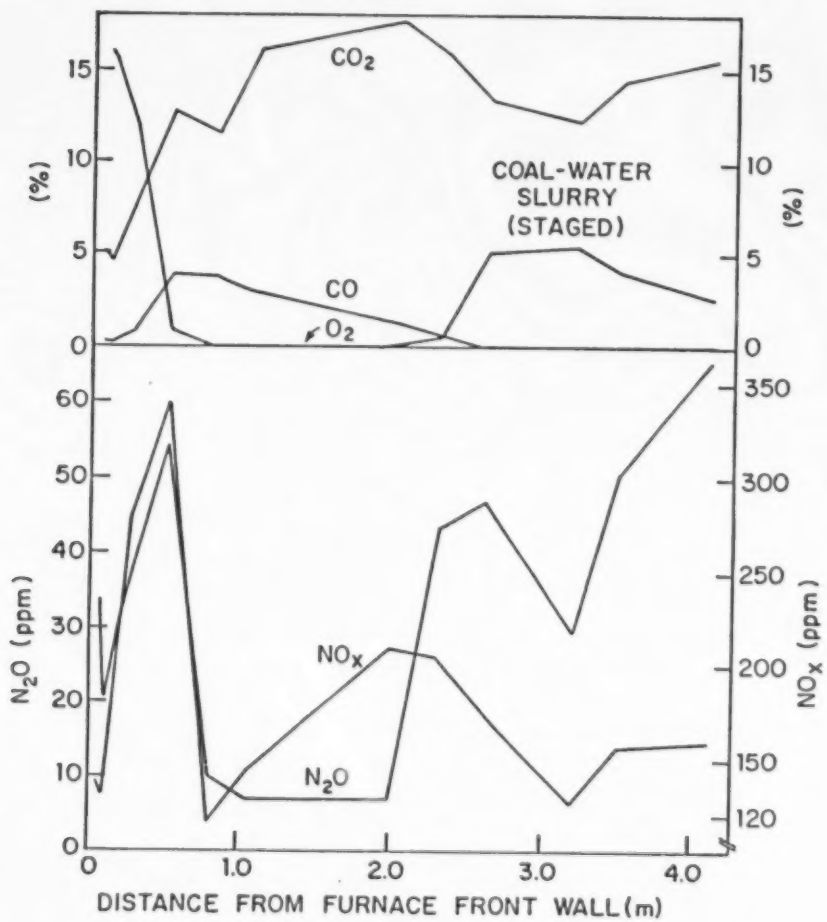


Figure 24. Centerline concentrations of O_2, CO_2, NO_x, and N_2O in MIT coal-water slurry fired combustion facility under staged conditions

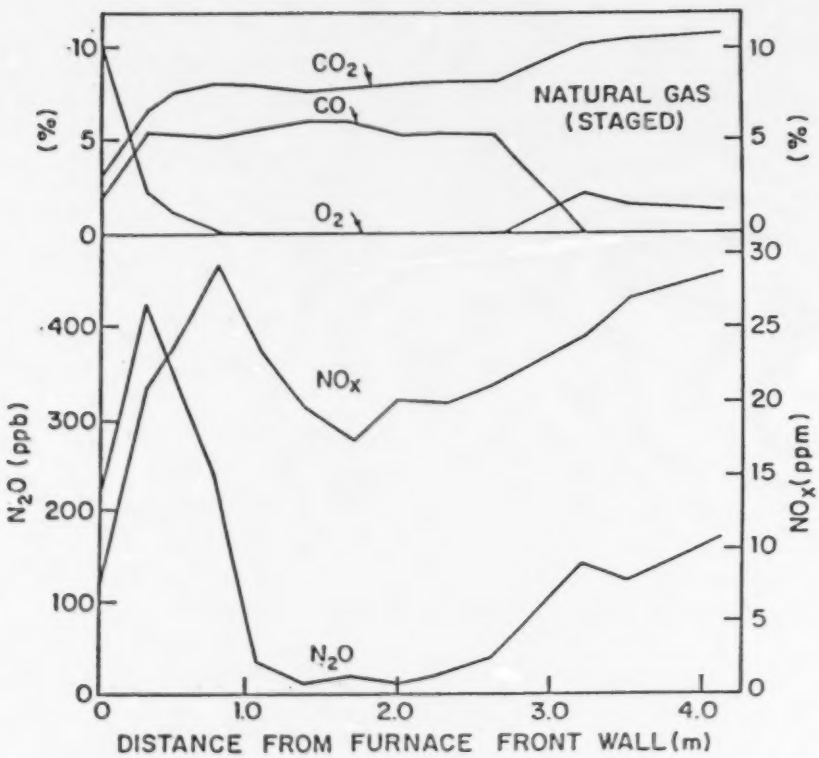


Figure 25. Centerline concentrations of O_2, CO_2, NO_x, and N_2O in MIT natural gas fired combustion facility under staged conditions

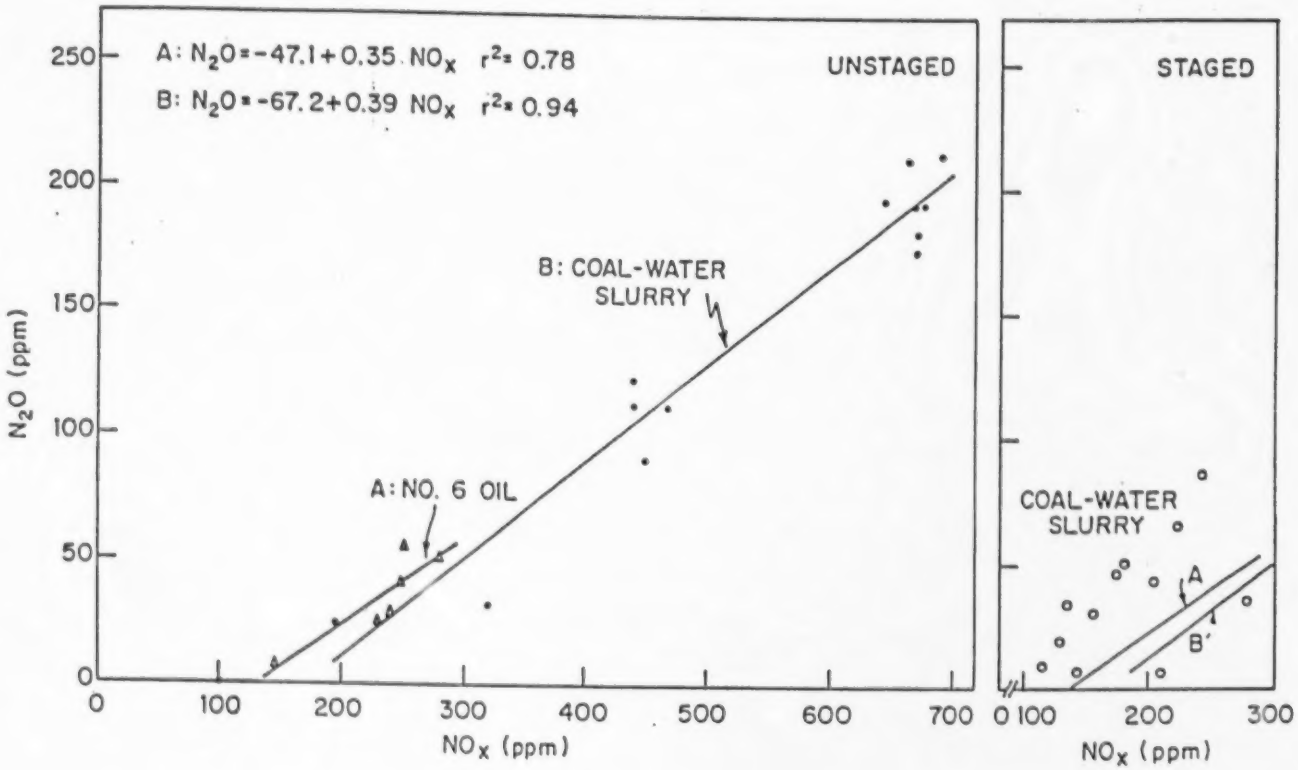


Figure 26. Exhaust N_2O and NO_x emissions under staged and unstaged conditions

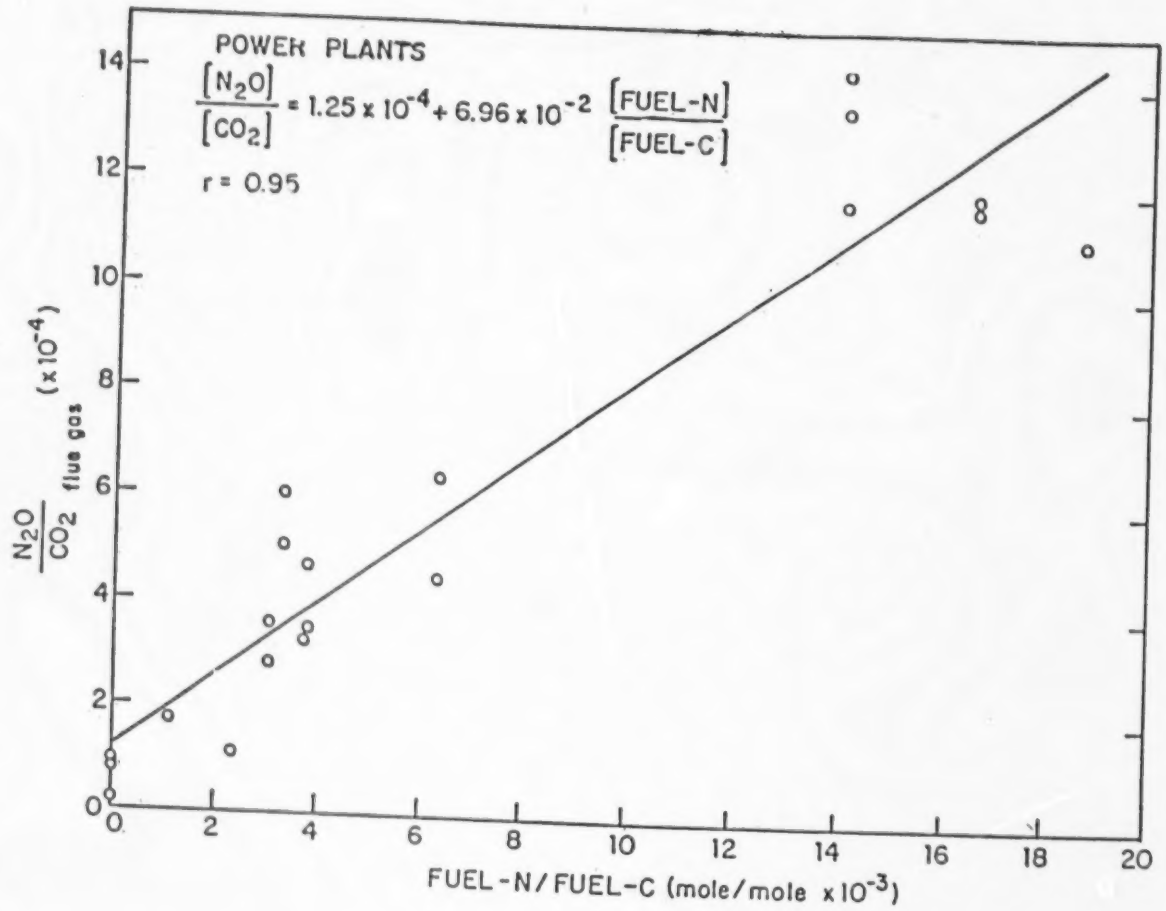
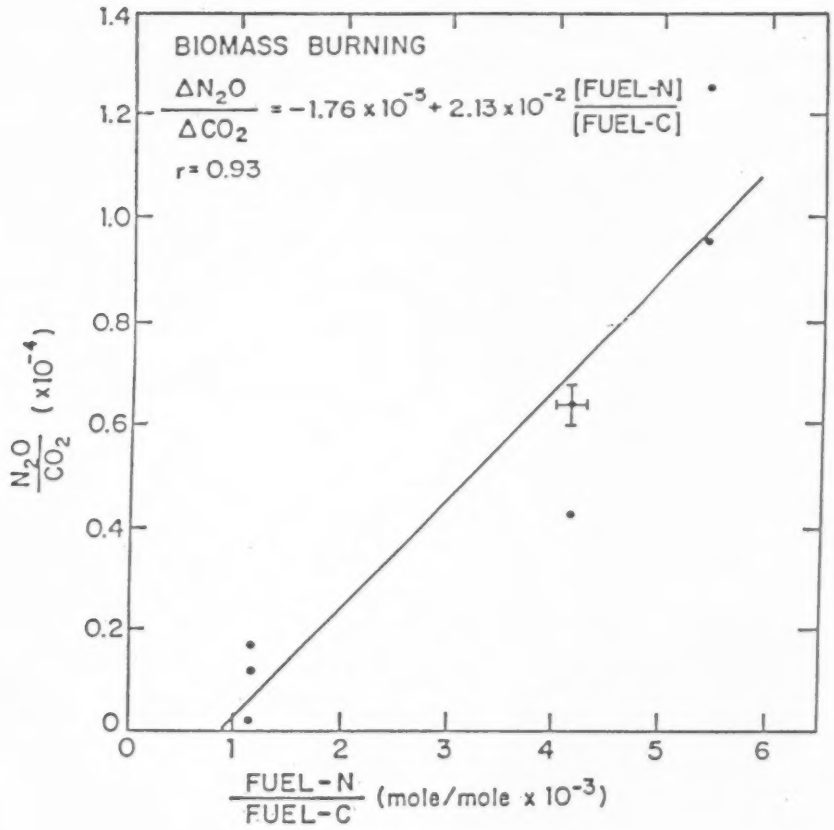


Figure 27. Relationship between N_2O emissions and fuel-nitrogen contents of natural gas, No. 6 oil and coal fired combustion systems

molar ratio of the fuel. Fig. 28 shows a similar correlation from experiments burning wood in bed type combustors. Both figures illustrate a high degree of correlation (based on the correlation coefficient) but also illustrate that the leading term in the correlation from biomass firing is an order of magnitude less than that found in the utility boiler trials. It was speculated that this difference, instead of reflecting a basic difference due to fuel chemical characteristics, was due to particle size and combustion environment effects.

Finally, Dr. Wofsy presented information from studies he had conducted concerning the N_2O global budget. In 1980, the atmospheric inventory was approximated to be 1500 Mtons N with a lifetime of 150 years, and a total annual input of 14+3 Mtons N/yr. He predicted that the contribution from combustion is 3.5+2 Mtons N/yr, with fertilizers accounting for 0.8 Mtons N/yr, which is consistent with results presented earlier in the workshop. Coal consumption patterns were presented which showed results similar to those presented by Mr. Kavanaugh. Dr. Wofsy gave predictions of the global N_2O production from fertilizers and fossil fuel combustion from 1860 to 2060, and he concluded with some predicted tropospheric N_2O concentrations for the same time frame. All predictions show N_2O production from anthropogenic sources increasing by more than a factor of four after 1960, reaching a level of 8 Mtons/yr in 2040. Exponential increase is expected for tropospheric N_2O concentration in the future.

Considerable discussion followed Dr. Wofsy's presentation, with attention focused on the mixing patterns and temperature profiles in the pilot scale facility. It was noted that final air addition under staged combustion conditions occurred at the 2.9 meter location. In Fig. 24, the effect of air addition on the CO, CO_2, and NO_x profiles is observed at the 1 meter location while actual presence of O_2 is detected at the 2.0 meter axial location. This implies that there is significant backmixing in this facility, especially considering the fact that the measurements were taken at the furnace centerline. This raised questions about the transverse temperature profiles and species concentration profiles. This suggested to Dr. Brown that N_2O formation was occurring on the periphery of the flame and being transported to other regions of the furnace. Although no firm conclusions were reached, it



Figuro 28. Relationship between N_2O emissions and fuel-nitrogen contents in burning ponderosa pine, oak log, and bark

was broadly agreed that further study was required, examining N_2O formation and destruction mechanisms.

As the final part of Session II, Dr. Zahniser (Aerodyne Research) presented a brief progress report on his study of N_2O formation kinetics. Those studies are both experimental and theoretical in nature with the experimental emphasis placed on determining the kinetic rate and product distribution from the NCO + NO reaction. The experiments are being conducted in a discharge flow tube reactor as illustrated in Fig. 29. The NCO radical is produced by a microwave discharge technique, and its concentration is monitored using laser induced fluorescence. N_2O and CO concentration is measured using tunable diode laser absorption. Different concentrations of NO were injected and the NCO, CO, and N_2O concentrations were measured as a function of distance. Fig. 30 shows first order decay plots for the NCO + NO reaction. The reaction rate developed in these experiments is consistent with results recently published by R. A. Perry.[17]

Dr. Zahniser has paid particular attention to the product distribution from this reaction considering both

$$NCO + NO \rightarrow N_2 + CO_2 \quad \text{and}$$

$$NCO + NO \rightarrow N_2O + CO.$$

At room temperature it has been found that approximately 40 percent of the NCO + NO collisions result in formation of N_2O.

Dr. Zahniser also presented results from a numerical modelling study simulating the pilot scale experiments discussed by Dr. Wofsy. The mechanism included 100 reactions in 20 species with temperature profiles constrained to be consistent with the experimental data. Table IX illustrates comparison of prediction and experiment. As shown, the predicted N_2O concentrations are on the same order as found experimentally but the NO_x predictions are substantially in error. It is also noted the N_2O predictions for coal and oil firing diverge significantly from the experimental results.

At the conclusion of Dr. Zahniser's presentation, there was considerable discussion on the actual N_2O formation and destruction mechanisms. The importance of rapid quenching, low temperature, availability of H and O atoms from the radical pool, and combustor design were discussed in relation to how they influence the rate of N_2O formation, preservation, and destruction. No major conclusions were drawn, but everyone agreed that this was a top priority area for further research. Much of the data did indicate a strong correlation

DISCHARGE-FLOW APPARATUS FOR NCO KINETIC MEASUREMENTS

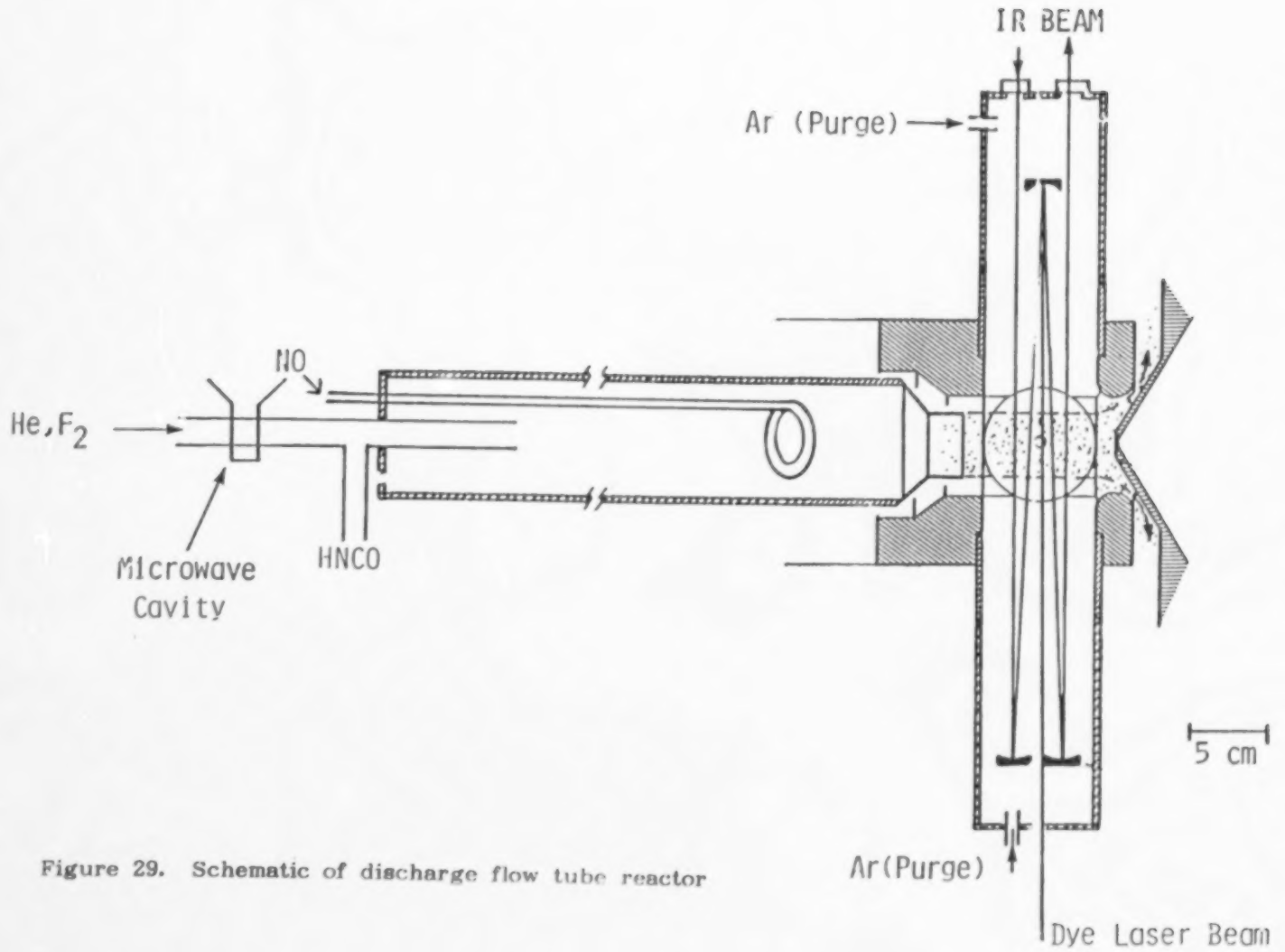


Figure 29. Schematic of discharge flow tube reactor

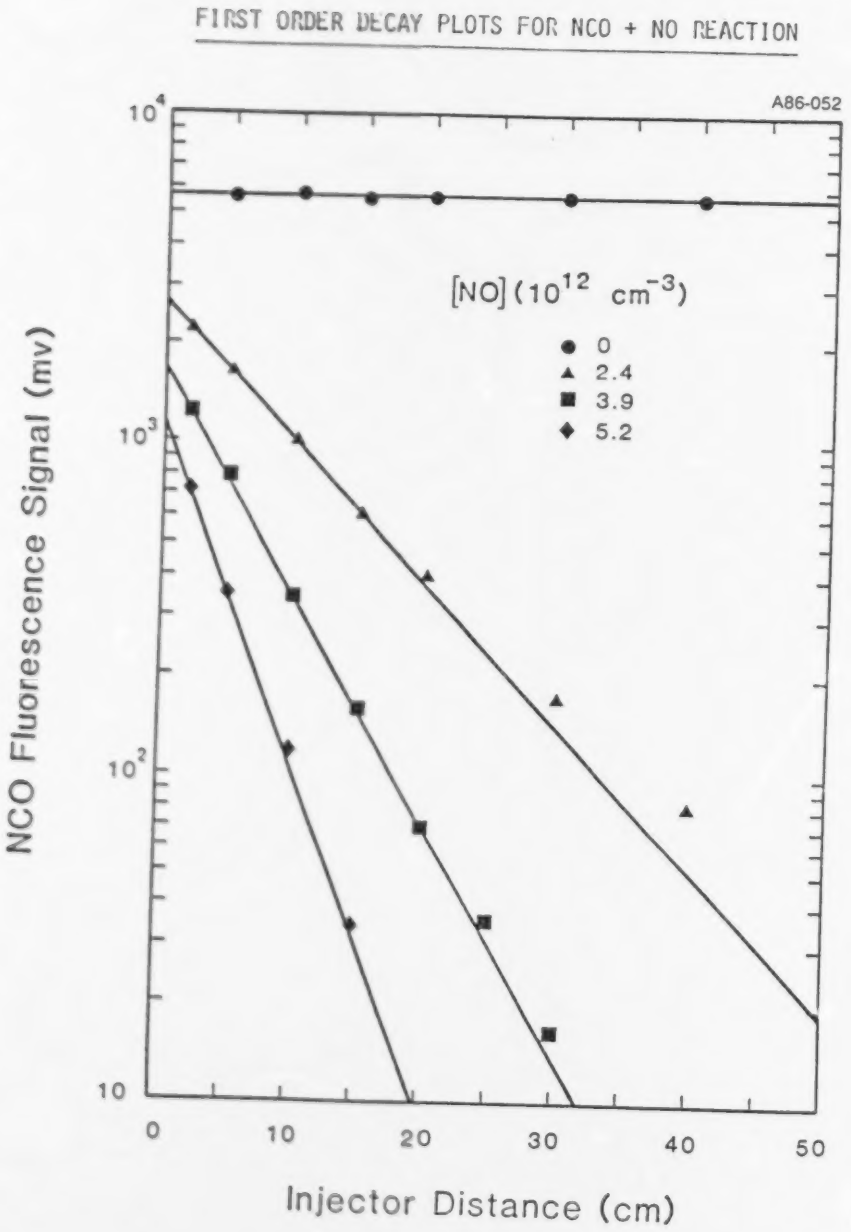


Figure 30. First order decay plots for NCO + NO reaction

Table IX. Comparison of numerical prediction and experimental results for NO_x and N_2O emissions

Flame Type	NO_x (ppm)		N_2O (ppm)	
	measured	predicted	measured	predicted
Natural gas	29	8	0.4	0.3
No. 6 oil	280	700	55	10
Coal	690	1900	210	110

note: Flame temperature is constrained to match data
($T_{max} \sim 1600°C$)

between N_2O and NO_x emissions. Consequently, a working hypothesis was presented that reducing NO_x would help reduce N_2O. This statement cannot be made in an absolute sense, but most participants agreed that it is probably true.

Dr. Brown was asked to summarize the discussion. She pointed out that research must continue in the five specific areas of field measurements, pilot scale testing, lab scale testing, modelling, and in studies of elementary reaction rates. In order to control N_2O emissions, it is necessary to understand the formation and destruction mechanisms. In particular, each researcher's goals must dictate the focus in his own experimentation and analysis. However, the diverse research community of the atmospheric scientists, combustion chemistry scientists, and others must keep in contact and be made aware of any advances in the various fields. This would allow them to perform complementary work which would be beneficial to all sectors of the scientific community.

At the conclusion of the session, Dr. Lanier summarized the discussion that had taken place by making a list of important issues and asked participants to state, in writing, whether they agreed or disagreed with the statement, and to comment on their opinion of the issues. The four statements he presented are listed below, along with the participants' responses.

Issue 1: Low NO_x burners will likely reduce N_2O.
(4-agree; 7-disagree; 3-neither)

The general consensus among the participants is that the existing data are too preliminary to be conclusive about N_2O reduction. A larger data base is necessary to substantiate any claims in this area.

Issue 2: Formation of N_2O is tied to low temperature oxidizing conditions (quenching).
(6-agree; 1-disagree; 4-neither)

Many participants state that this seems likely, but data are quite preliminary here too. Some experimental work has given indications that the oxidizing conditions either cause N_2O to be formed or prevent it from being destroyed.

Issue 3: We do not know the chemistry and fluid mechanics well enough to predict how combustion modification will affect N_2O emission.
(12-agree; 1-disagree)

Practically everyone is in agreement, stating that more fundamental research

is necessary before combustion modification programs can be implemented. Some suggestions for further study include developing a model which incorporates flame dynamics of the cooler flame regions and examining the results from high quench experiments such as flat flame burners.

Issue 4: The R & D program should include fundamental and field evaluation components, and the results must be integrated.
(14-agree)

There is total agreement on this statement, although some would like to see an emphasis on fundamental research and others on a more comprehensive field testing program.

TECHNICAL SESSION III--SOURCE PRIORITIZATION

This session of the workshop was concerned with the mobile and stationary source emissions of N_2O. It was included to help identify the source types with the largest global emission of N_2O, which helps EPA prioritize R&D activities on the global level of atmospheric N_2O, in order to prioritize the focus of EPA's R&D activities.

The discussion leader of the first part of Session III was John Sigsby of the Mobile Source Emissions Branch of EPA's Atmospheric Sciences Research Laboratory. Mr. Sigsby's presentation examined the N_2O emissions from mobile sources and their relative contribution to the global N_2O emission flux. He began with a description of the studies which were performed in EPA's emissions testing laboratory. The two main parameters examined in their testing included (1) variation of vehicle type and condition, and (2) variation of driving conditions. Studies examining the first parameter involved comparisons between diesel and gasoline powered vehicles, high mileage and low mileage vehicles, those equipped with and without catalysts, and among trucks, buses, and passenger cars. The variation of driving condition included varying temperature and driving schedule. Five driving schedules were simulated. These are listed below, along with the average vehicle speed of each cycle. (Specific cycle speed records are included in Appendix D.)

(1)	Federal Test Procedure Cycle (FTP)	19 mph
(2)	Sulfur Emissions Test Cycle (SET)	35 mph
(3)	Highway Fuel Economy Cycle (HWFET)	45 mph
(4)	New York City Cycle (NYCC)	7 mph
(5)	Heavy Duty Transient Cycle (HDTC)	19 mph

Fig. 31 is a schematic drawing of the test equipment and sampling procedure used by EPA. Similar sampling equipment was used by Southwest Research in collecting comparable data. The laboratory simulation included an electric chassis dynamometer to simulate road load and inertia conditions, and testing conducted in an insulated cold cell to allow for variation in ambient temperature. A constant volume sampler was used to dilute and cool the exhaust prior to sampling. Emission samples were collected in Tedlar bags and analyzed by GC/ECD within 15-20 minutes.

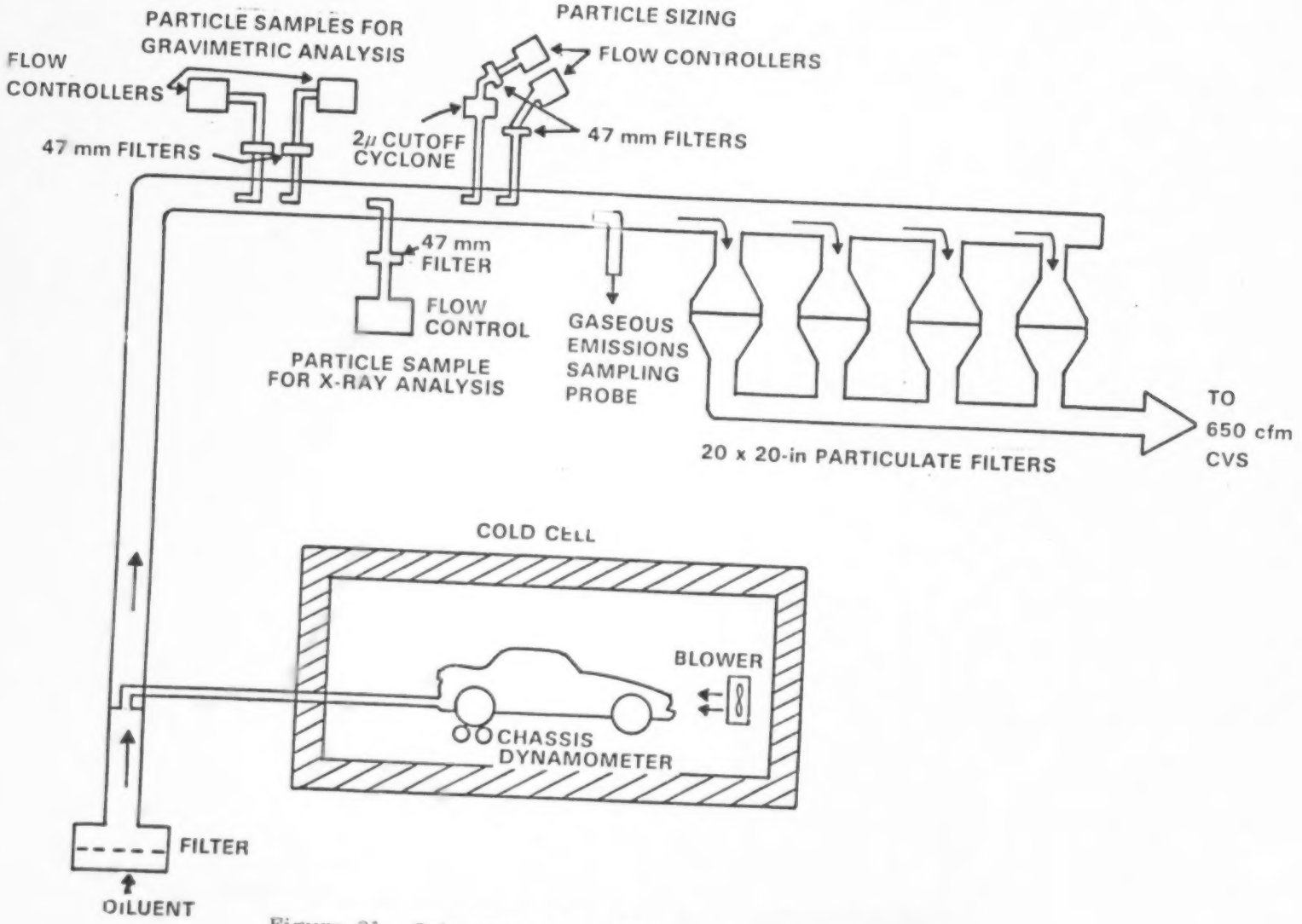


Figure 31. Schematic of mobile source emissions testing procedure

Table X, which specifies the four categories of vehicle types used, gives the results from the emissions tests. The numbers enclosed in parentheses represent the number of vehicles tested, and the emission rates (in mg/mi) are given as a range. Mr. Sigsby noted that the cars equipped with catalysts showed a wide range of emission rates. A value of 100 mg/mi was chosen as a conservative estimate of the median. It is important to note that only one non-catalyst vehicle was tested. The statistical validity of one vehicle is obviously poor, so even though the tests predicted that vehicles which are not equipped with catalysts have lower emission rates, no definitive conclusions can be drawn until further testing is performed. Table X also specifies the parameters which appear to influence emission rates. These include inertia (vehicle size), driving cycles, engine/emission control malfunction, and the presence or absence of a catalyst. No clear trend was observed from variation of ambient temperature.

Based on the above results, preliminary estimates of the national and global N_2O emission flux from mobile sources can be determined. As a conservative estimate, it can be assumed that the average emission rate for vehicles in the United States is 100 mg/mile. Based on a 1982 estimate, the assumed vehicle fleet size in this country was 115 million, and the total vehicle miles travelled were approximately 1.6×10^{12}. Therefore, the total U.S. production of N_2O from mobile sources that year was on the order of 1.6×10^{5} metric tons. In an earlier presentation by Dr. Weiss, it was estimated that the anthropogenic emission of N_2O was on the order of 3.0×10^{6} metric tons (as N_2O) per year. Thus, it can be concluded that the N_2O emission rate from U. S. mobile sources is approximately 5-5.5% of the total N_2O emission rate from anthropogenic sources. Based on this comparison, it appears that U. S. mobile sources represent an insignificant N_2O emission source. Mr. Sigsby also predicted that vehicle use in the rest of the world will significantly increase in the future, but that the majority of those vehicles will probably not be equipped with catalysts. Based on the available data, vehicles without catalysts appear to have a significantly lower emission rate than those with catalysts. It was therefore concluded that even with future increased auto use in other countries, mobile sources will probably have little impact on atmospheric N_2O loading.

Table X. N_2O emission rates from mobile sources, and some influencing factors
Sources: See references 1-5.

N_2O EMISSION RATES

non catalyst car (1)	5 - 6 mg/mi
catalyst cars (22)	7 - 137 mg/mi
diesel trucks/buses (4)	31 - 147 mg/mi
gasoline trucks (2)	48 - 97 mg/mi

Factors Influencing Emission Rates

- Inertia i.e. vehicle size

  trucks > passenger cars

- Driving cycles

  NYCC > FTP > SET > HWFET

- Engine/Emission Control Malfunction

  worst case, (disabled EGR)
  factor of three increase

- Catalyst

  catalyst > non catalyst
  (non catalyst based on 1 vehicle)

- Ambient temperature

  influence not clear

During this session, questions were also raised concerning N_2O emissions from gas turbines, particularly emissions from military aircraft, which are capable of flying in the boundary layer between the troposphere and the stratosphere. If significant levels of N_2O were exhausted into the atmosphere at this level, the effect on the ozone layer could be important. Ms. Mary Marx, from the U. S. Naval Propulsion Center, indicated that a very small portion of the military air miles are flown at such heights; most military air miles are travelled at the height of commercial aircraft which is approximately 30,000-40,000 feet. It was generally agreed that N_2O emissions from aircraft (of any kind) do not appear to significantly affect the atmospheric N_2O levels.

Following the break between the mobile source and stationary source portions of session III, Dr. Herb Wiser, the senior science advisor for EPA, gave a short presentation on the history of N_2O research and its current status. He also provided the participants with a complete overview of the effect of N_2O on the ozone layer. Much of the information he presented was incorporated into the introduction of this report and will not be repeated here. Dr. Wiser also stated that an interagency committee was formed to look into the N_2O research program and other similar areas of interest. The committee is called the National Climate Program, and the agencies which participate in the committee include the National Oceanographic and Atmospheric Administration (NOAA), the National Aeronautic and Space Administration (NASA), the National Science Foundation (NSF), the Department of Energy (DOE), and the Environmental Protection Agency (EPA). The purpose of the committee is to examine potential avenues of future research, and to decide which agency is best equipped for the chosen tasks.

The second half of Session III, which concerned stationary sources of N_2O, was led by Mr. Carlo Castaldini of Acurex Corporation. Mr. Castaldini presented results from EPA-sponsored field test studies of different stationary sources fired with different fuels, including both external and internal combustion sources. Table XI presents a summary of emission results from external combustion sources while Table XII presents a similar listing for internal combustion sources. Fig. 32 is a plot of N_2O vs. NO_x levels based on the data in Table XI. The data show a wide range of N_2O levels, (7-110 ppm) with the N_2O:NO_x ratios ranging from 10-42 percent. Despite the

Table XI. N_2O emissions from external combustion sources

SOURCE/FUEL/OPERATION	NO. OF SAMPLES	N_2O (PPM)	NO_x (PPM)	N_2O/NO_x (PERCENT)	O_2 (PERCENT)
• FIRETUBE STOKER BOILER					
-- COAL	1	28	140	20	6-9
-- COAL AND PET	1	61	145	42	3-8
• WATERTUBE BOILER					
-- COAL/WATER SLURRY (CWS)	3	18-98 (54)	397	14	6.6-7.0
-- COAL/OIL MIXTURE (COM)	1	69	376	18	3-4
-- COAL/WATER SLURRY (CWS)	2	29-35 (31)	234	13	2-3
-- COAL/WATER SLURRY (CWS)	2	45-110 (81)	327	25	2-3
• OIL-FIRED ENHANCED OIL RECOVERY STEAMER					
-- WITH EPA LOW-NO_x BURNER	1	7	70	10	2-3
-- WITH MHI LOW-NO_x BURNER	3	13-21 (17)	106	16	2-3

Table XI. N_2O emissions from external combustion sources (continued)

SOURCE/FUEL/OPERATION	NO. OF SAMPLES	N_2O (PPM)	NO_x (PPM)	N_2O/NO_x (PERCENT)	O_2 (PERCENT)
• GAS/OIL-FIRED REFINERY CRUDE OIL HEATER					
-- UNCONTROLLED	1	47	162	29	3 TO 4
-- WITH STAGED COMBUSTION NO_x CONTROL	1	27	116	23	3 TO 4
• GAS/OIL-FIRED WATERTUBE BOILER					
-- UNCONTROLLED	1	53	239	22	2 TO 3
-- WITH NONCATALYTIC NO_x REDUCTION BY NH_3	1	17	141	12	2 TO 3
	17 TOTAL	41 AVERAGE	204 AVERAGE	20 AVERAGE	

Table XII. N_2O emissions from internal combustion sources

SOURCE/FUEL/OPERATION	NO. OF SAMPLES	N_2O (PPM)	NO_x (PPM)	N_2O/NO_x (PERCENT)	O_2 (PERCENT)
• GAS-FIRED RICH-BURN RECIPROCATING ENGINE					
-- UNCONTROLLED	2	65-180 (123)	2700	4.6	3
-- WITH NONSELECTIVE CATALYST	2	18-56 (37)	2700	1.4	2
• GAS-FIRED LEAN-BURN RECIPROCATING ENGINE					
-- UNCONTROLLED	1	98	2600	3.8	11
-- WITH SELECTIVE CATALYST/NH_3	1	43	490	8.8	11
	6 TOTAL	75 AVERAGE	2100 AVERAGE	4.7 AVERAGE	

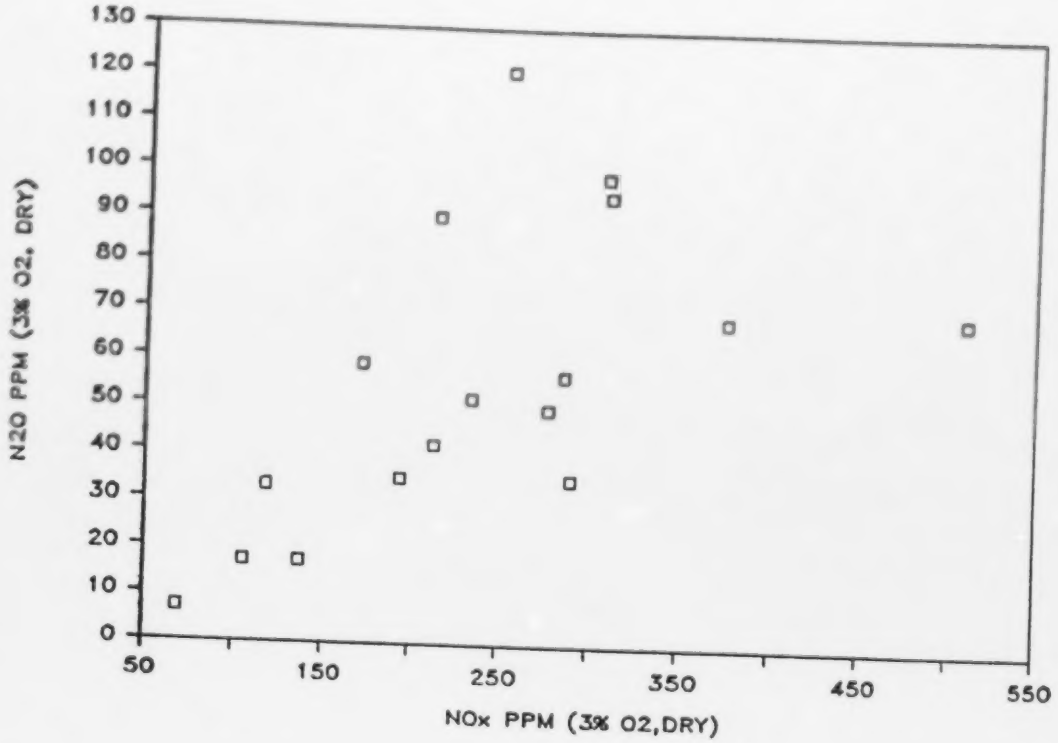


Figure 32. N_2O and NO_x emissions from various sources

apparent lack of consistency in N_2O:NO_x ratios, it does appear from the data that when NO_x controls were applied to specific sources, the N_2O levels were reduced accordingly. It is interesting to note from the data in Table XII that the N_2O levels were significantly reduced when catalytic NO_x controls were added to IC engines firing gasoline. This is an opposite trend from the mobile source results presented earlier by Mr. Sigsby, although it must be noted that these results are steady state emissions, while the mobile source data are transient, and control technologies for each are completely different.

Fig. 32 is an updated version of Fig. 17 presented earlier in the session by Dr. Lanier and contains several recently acquired data points. These recent data points significantly increase the apparent scatter relative to that indicated by Fig. 17. In fact, the correlation coefficient (R^2) for a straight line curve fit to Fig. 32 is only 0.33. Dr. Wofsy suggested that part of the apparent scatter could be the result of including data from stoker fired boilers. In the Harvard tests, such units exhibited a much lower N_2O:NO_x ratio (see Fig. 28). Table XI indicates, however, that in the Acurex tests, coal plus PET fired in a stoker boiler resulted in the highest N_2O:NO_x ratio (42 percent). Mr. Castaldini stated that, having performed emissions tests at 17 different sites, it was difficult for him to see a common denominator to any of them. Discussion among participants addressed a wide range of potential parameters including fuel-bound nitrogen effects, fuel volatility, boiler excess air levels, and stoker versus disperse phase combustion systems.

Mr. Castaldini then summarized the discussion which had taken place. He stated that it is important to make a distinction between various combustion sources rather than to accept an across-the-board N_2O:NO_x ratio of 25-30 percent. (This is the approach used earlier by Dr. Kavanaugh.) He pointed out that the data from the internal combustion engines show that the NO_x emissions are greater than those from boilers, but that the exhaust N_2O concentrations are approximately the same for internal and external combustion. And finally, his evaluation shows that some catalysts may enhance N_2O formation while others may hinder it. As in technical Session II, a summary of the session was presented in statement form for the workshop participants to respond to. The four summary statements and a summary of participant responses is presented below.

Issue 1: The diversity of mobile and stationary source types requires more representative N_2O data.
(11-agree; 2-neither agree nor disagree)

More data are definitely needed to examine the impact of stationary and mobile emissions and possible control strategies. A field or lab data acquisition program needs to be defined based on available data from anthropogenic sources, though piggybacking should be used where possible, since testing is expensive. Particular areas to be studied include different fuel and boiler types.

Issue 2: Post-combustion catalytic reactions on N_2O formation/destruction are unclear.
(11-agree; 2-neither agree nor disagree)

Most participants state that this is certainly an area for more study, and much valuable information could be gained from a small effort. If correlations could be found for certain parameters such as fuel type, combustor type, and operational characteristics, more specific applications of all catalyst types might be found.

Issue 3: Combustion modification controls should be investigated as a promising N_2O abatement strategy.
(5-agree; 4-disagree; 3-neither)

The general opinion, even by those who agreed with the issue statement, was that the modifications for control should not be examined until more information is known about N_2O destruction/formation. Combustion modifications could be helpful when the results from modeling and fundamental measurements indicate the direction the control strategy should take.

Issue 4: Research should focus on stationary, energy intensive sources.
(4-agree; 1-disagree; 4-neither)

Most participants feel that the highest priority research should be in the area of highest N_2O emissions, which appear to be stationary sources. However, some of the participants suggested that piggyback testing be performed in all EPA-sponsored research. A few participants felt that the data base must be expanded before deciding which research area to concentrate on.

Prior to initiating the fourth and final technical session, discussion ensued on EPA's role in prioritizing research needs. Some participants feared that EPA may be stifling creativity by financially supporting only the "most important" research areas. Dr. Wiser (EPA) responded that the Atmospheric Chemistry & Physics Committee, which is composed of representatives of industry and academics, reviews unsolicited proposals and gives recommendations to the EPA budget committee, which in turn provides funding to any non-profit organization. Therefore, no research area or group will be denied funding if the proposed work is deemed worthwhile.

TECHNICAL SESSION IV--CONTROL STRATEGIES

The final session of the workshop was originally intended to aid EPA in developing emission control approaches for the most important N_2O emission sources. However, the vast majority of potential control strategies had been discussed in earlier sessions. This session, then, summarized the entire workshop in terms of suggestions for action upon the issues which had been discussed during the previous sessions.

Mr. R. E. Hall and Mr. Joseph McSorley, (EPA - Combustion Research Branch) were discussion co-leaders for this session. Mr. Hall began his presentation by describing some of the current NO_x emission control strategies. One of the most popular technological methods currently applied is termed reburning. With reburning, the amount of primary fuel injected to the burner is reduced, creating a lean burning zone in the initial stages of a furnace. When the burning is partially complete, more fuel is injected, creating a fuel-rich zone, and then air is injected to complete the burnout. It is because of this secondary fuel addition that many of the nitrogenous species are converted to N_2. Other NO_x emission controls are in use today as well, some being applied to fuel NO_x and others to thermal NO_x. In all cases, an important issue is whether control strategies which are currently being applied for NO_x control would be applicable for N_2O control. The key factor in being able to answer the question is one of fundamentals. If the basic N_2O formation and destruction mechanisms are known, the approaches to controlling its formation would be straightforward. Therefore, before numerous tests are conducted to determine a specific control modification's effectiveness, the basic nature and characteristics of N_2O should be determined. Currently available data do, however, contain much information about N_2O along with NO_x. These data can be studied to glean information concerning NO_x emission controls applied to N_2O emission control. Mr. Hall cautioned the across-the-board application of NO_x controls for N_2O, for it was shown that some catalysts which were applied for reducing NO_x emissions actually served to increase emissions of N_2O.

Discussion on "piggybacking" of current testing programs followed; extra data specifically for N_2O should be gathered along with the test data from NO_x studies and other experimental programs. This would serve to augment the current data base without requiring extensive expenditures. In most cases,

N_2O and NO_x levels tend to correspond; i.e., NO_x controls are effective in reducing N_2O emissions. There is no evidence, however, that other control approaches can be used which have not been examined yet. It must be realized that the environmental effects of N_2O and NO_x are different too, and each one requires further investigation. N_2O emissions contribute to the problem of depletion of the ozone layer and global warming, whereas NO_x emissions are one of the key factors in the formation of acid rain.

Again, the session was summarized with five statements presented to the participants. The five statements and participant responses are presented below.

Issue 1: Fundamental combustion research is needed to determine the mechanisms for N_2O formation/destruction.
(4-agree)

All participants agree with this statement. Specifics mentioned for further study include fuel type (oil, coal, or gas) and its nitrogen content; operating parameters such as temperature, A/F ratio, and pressure; and different combustor types. One person suggested that FCR is only necessary if N_2O from combustion is a significant contribution to the global budget.

Issue 2: Initially, emphasis should be placed on FCR with its output used to provide directions for field tests.
(2-agree; 2-neither agree nor disagree)

One participant's suggestion is to examine current data, make preliminary field tests on the basis of that, and then FCR can be applied to the results of the field test. Another participant believes that full scale testing is necessary, and should only cost about $15K per site.

Issue 3: Some classical NO_x control techniques may be effective N_2O control measures, but research is needed to determine which ones.
(3-agree; 1-neither agree nor disagree)

Some specific control techniques mentioned which may be effective for N_2O control are selective catalyst reduction, flue gas recirculation, low NO_x burner technologies, and reburning. The extent of this control capability is not clear, however, especially with respect to clean (low N) fuels. One

participant suggests that, right now, accurate data are not needed, but an order of magnitude estimate would be helpful.

Issue 4: Exhaust catalysts are effective control devices but catalyst composition is critical.
(3-agree; 1-neither agree nor disagree)

If control is necessary, mobile source emissions seem to be more greatly affected by catalysts than stationary sources do. Current catalytic materials such as the noble metals, vanadium, Fe/Cr, and other zeolites and perovscites should be evaluated to assure that when N_2O is reduced, other hazardous pollutants such as nitropyrenes are not promoted in the catalytic reaction. It should be noted that vehicles today are already equipped with noble metal catalysts for hydrocarbons, NO_x, and CO, as required by law.

Issue 5: Field sampling should be ongoing via in-house tests and piggyback testing under contract and should be coordinated with others.
(4-agree)

All participants agree that more testing should be done to expand the data base. Suggestions are made that EPA be an organizer of an interagency/ academic consortium of researchers in the area of combustion emissions. A formal task force can be formed to generate, validate, and evaluate N_2O data.

CONCLUSION

The foregoing material documents the numerous presentations and follow-up discussions for the workshop. A wide range of topics and critical issues were discussed among a group of individuals with diverse backgrounds. Perhaps the best evaluation of the workshop's success was that practically every attendee stated that he or she had received information which would be beneficial to his or her ongoing research studies. In sponsoring this workshop, EPA sought information to help establish priorities for a potential R&D program on combustion generated N_2O emissions. To that end, the workshop was formatted around a series of questions which were perceived (a priori) to be critical. Some of the questions were answered. For the unanswered questions, there is an appreciation for the complexity of N_2O combustion phenomena. At the very least, the workshop sponsors now know the questions to ask--a critical requirement for formulating an effective R&D program. The following presents a brief summary of key workshop conclusions.

(1) For N_2O concentration levels typically observed in boiler exhausts, analysis by GC/ECD appears to be the most cost effective approach. There are numerous sources of potential measurement error which should be avoided but, with care, the technique can yield reliable results. Efforts are underway to develop alternate techniques such as a continuous N_2O monitor which would be of significant benefit for combustion source measurement.

(2) There are many conflicting results concerning the interrelation of N_2O and NO_x emission rates. There is a significant body of evidence suggesting that reducing NO_x emissions tend to reduce N_2O emissions. This suggests that currently available or emerging NO_x combustion modification control techniques might be effective in reducing N_2O emissions. There is a clear need, however, for a better understanding of how combustion process parameters influence the N_2O formation and destruction process.

(3) There are only limited data available for N_2O emission rates from mobile sources. These appear to be insignificant contributors to the total anthropogenic N_2O emission flux. The data base for non-catalyst equipped automobiles currently consists of one datum point. A significant expansion of that data base is called for. A potential approach might be through cooperation with foreign governments who do not require emission control catalysts.

(4) The dominant source of N_2O combustion emissions appears to result from burning fuels with high bound-nitrogen content. On that basis, research emphasis should be placed on coal and heavy residual oil-fired boilers.

(5) Long term projections of significant growth in global N_2O emission rates should be considered preliminary since the available data base is insufficient for developing reliable emission factors. Such projections are important tools for development of governmental policy and thus development of reliable emission factors should be an important component of an EPA R&D program.

The final conclusion from the workshop is that the February 13-14 meeting opened a constructive dialogue among a diverse group of professions. It is the strong opinion of the current author (mirrored by many other participants) that this dialogue should be continued.

ENDNOTES

[1]C.M. Urban and R.J. Garbe, "Regulated and Unregulated Emissions from Malfunctioning Automobiles," SAE 790696, June, 1979.

[2]L.R. Smith and F.M. Black, "Characterization of Exhaust from Passenger Cars Equipped with 3-Way Catalyst Control Systems," SAE 800822, June, 1980.

[3]H.E. Dietzmann, M.A. Parness, and R.L. Bradow, "Emissions from Trucks by Chassis Version of 1983 Transient Procedure," SAE 801371, October, 1980.

[4]H.E. Dietzmann, M.A. Parness, and R.L. Bradow, "Emissions from Gasoline and Diesel Delivery Trucks by Chassis Transient Cycle," ASME Energy-Sources Technology Conference, Houston, TX., January, 1981.

[5]J.N. Braddock, "Impact of Low Ambient Temperature on 3-Way Catalyst Car Emissions," SAE 810280, February, 1981.

[6]L.R. Smith and P.M. Carey, "Characterization of Exhaust Emissions from High Mileage Catalyst-Equipped Automobiles," SAE 820783, June, 1982.

[7]Gregg Marland, "Anthropogenic Impacts on the Atmospheric Concentration of Nitrous Oxide," Institute for Energy Analysis, Oak Ridge Associated Universities, Oak Ridge, TN, 1985.

[8]Ibid.

[9]V. Ramanathan, et al., "Trace Gas Trends and their Potential Role in Climate Change," J. Geophysical Research, Vol. 90, No. D3, 20 June 1985, pp. 5546-5547.

[10]D. Pierotti and R. A. Rasmussen, "Combustion as a Source of Nitrous Oxide in the Atmosphere," Geophysical Research Letters, Vol. 3, No. 5, May 1976, pp. 265-267.

[11]R. F. Weiss and H. Craig, "Production of Atmospheric Nitrous Oxide by Combustion," Geophysical Research Letters, Vol. 3, No. 12, Dec 1976, pp. 751-753.

[12]C. Castaldini, et al., "Environmental Assessment of an Enhanced Oil Recovery Steam Generator Equipped with a Low-NO_x Burner, Volume I," EPA-600/7-86-003a (NTIS PB86-159837), February 1986.

[13]R. F. Weiss and H. Craig, "Production of Atmospheric Nitrous Oxide by Combustion," Geophysical Research Letters, Vol. 3, No. 12, Dec. 1976, pp. 751-753.

[14]J. C. Kramlich, et al., "Behavior of N_2O in Staged Pulverized Coal Combustion," Combustion and Flame, Vol. 48, No. 1, Oct. 1982, pp. 101-104.

[15]R. A. Perry, "Kinetics of the Reactions of NCO Radicals with H_2 and NO using Laser Photolysis-Laser Induced Fluorescence," J. Chem. Phys., Vol. 82, No. 12, 15 June 1985, pp. 5485-5488.

[16]G. C. England, et al., "Mechanisms of NO_x Formation and Control: Alternate and Petroleum-Derived Liquid Fuels", 18th Symposium (International) on Combustion, The Combustion Institute, 1981.

[17]R. A. Perry, "Kinetics of the Reactions of NCO Radicals with H_2 and NO using Laser Photolysis-Laser Induced Fluorescence," J. Chem. Phys., Vol. 82, No. 12, 15 June 1985, pp. 5485-5488.

Appendix A

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

December 23, 1985

Dear :

Your are invited to participate in an EPA workshop on nitrous oxide emissions scheduled for February 6-7, 1986. As a result of a recent Global Atmospheric Workshop held in November 1985, the U. S. Environmental Protection Agency has become increasingly concerned about the importance of N_2O emissions to the environment. Available data indicates that atmospheric N_2O concentration is increasing by approximately 0.25 percent per year. Since this species has an atmospheric lifetime of approximately 100 years, it is evident that current N_2O emissions are in excess of historic anthropogenic levels. The fact that N_2O is an important greenhouse gas and that it is persistent in the atmosphere makes it important for EPA to estimate future N_2O emission rates and ambient concentrations and to identify control strategies for possibly modifying these trends. To reach that goal, it is necessary to understand the sources of N_2O emissions, to understand the factors which control source emission rates, and possibly to identify techniques for minimizing emissions.

Evidence from research funded by EPA's Office of Research and Development as well as results from other agencies indicate that combustion of fossil fuel may be an important source of the atmospheric N_2O concentration growth. The data base on the N_2O emission rate from combustion sources is limited and not sufficiently reliable to develop emission factors or to formulate potential control strategies.

There are some atmospheric scientists and combustion experts who are deeply interested in this area but there has been very limited interchange of information between them. As an initial step, EPA will be sponsoring a workshop in early February 1986. The purpose of this workshop is to bring together a limited number of experts to help EPA develop a research strategy for systematically reducing uncertainties and filling in the critical data gaps as rapidly as possible. You have been identified as one of the key individuals in the United States who is knowledgeable in this area and are invited to participate in the workshop. It should be emphasized that EPA is planning this workshop for the development of a research strategy. You will have an opportunity to provide your most current thoughts on the state of knowledge and understanding of N_2O emissions that affect the global atmospheric processes.

A date for the workshop has been tentatively set for February 6 and 7, 1986, with the meeting to be held at the EPA's Environmental Research Center in Research Triangle Park, N.C. EPA feels that it is important to secure input from key individuals, such as you, but also recognizes that this date is not far away. An alternate date of February 13 and 14 may possibly be offered if the 6th and 7th conflicts with your schedule. Enclosed you will find a reply form and return envelope for you to indicate your willingness to attend the workshop and a block to check which dates you would prefer. We request that you return your reply as rapidly as possible and if possible call Dr. Steve Lanier no later than January 13, 1986.

The workshop is being coordinated by Energy and Environmental Research Corporation (EER). If you have any questions about the workshop or need assistance in arranging travel, please contact Dr. W. Steven Lanier of EER by phone at (919) 489-1726. A block of rooms has been reserved at the Sheraton University Center in Durham, North Carolina.

EPA sincerely hopes that you can participate in the workshop and that the meeting will be mutually beneficial.

Sincerely,

Joseph A. McSorley
Combustion Research Branch (MD-65)
Air and Energy Engineering Research Laboratory

Enc.

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Appendix B

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

February 3, 1986

Dear :

We are pleased that you have agreed to take time from your schedule to participate in our N_2O workshop. Over the past week we have attempted to contact each of you to confirm the meeting date (February 13 and 14) and to inform you that the workshop will be held at the Sheraton University Center instead of the EPA Environmental Research Center. For your itineraries, the Sheraton University Center is located at 2800 Middleton Avenue and the telephone number is (919) 383-8575. The Sheraton University Center offers free shuttle service from the airport if you call when you arrive.

Attached to this letter you will find a tentative agenda for the two-day workshop and a list of participants. As noted, the workshop is divided into four discussion sessions. Preceding the first session, there will be a series of opening remarks designed to place the issue of N_2O emissions into a global context.

Dennis Tirpak and Mike Cavanaugh will discuss EPA's view of the global N_2O and O_3 issues. These introductory remarks are the only presentations to be given in a conference-type format.

Following the introductory/overview remarks, the WORKshop sessions will begin. Before describing the thrust/content of each session, it is important that you understand the working format which has been adopted. Each session will deal with a particular aspect of fossil-fuel combustion-generated N_2O research. We recognize that there are other major N_2O emission sources such as agricultural denitrification, biomass burning, N_2O manufacturing, lightning, etc., but these are being evaluated by other research programs sponsored by NOAA, NASA, NCAR, etc. The intent is to raise a series of critical issues and to obtain input from the assembled experts. We are fully aware that a diversity of opinions may be held on any or all of the issues to be raised. Hearing each of your opinions and understanding why you hold that opinion is the real reason for the workshop.

Each session will have a discussion leader who will present some critical issues and provide his opinions on those issues. Then, each participant will have an opportunity to share his/her views in an informal round-table discussion. You may agree or disagree with any part of the discussion leader's opinion. Each of you have valuable information and insights and EPA wants the benefit of your experience in formulating its research program. At the end of each session, the discussion leader (or one of the workshop organizers) will write on a blackboard his/her perception of the "consensus" opinion expressed by the group as well as a priority list of research needs. In addition, each of you will be given a worksheet for each session and asked to comment on how you integrate the various information presented. You may agree, disagree, or modify the "consensus opinion" written on the board. You may also wish to modify, delete, rearrange, or agree with the listed research priorities. These worksheets eliminate the need for any written follow-up by the participants and will be used by EPA in preparation of a workshop summary report.

As a final note on workshop operational detail, it should be noted that a wide variety of topics are to be covered and we want to hear any input you may have on each subject area. The amount of time available is limited and thus long presentations of research results is discouraged. We want you to think about the critical issues in each session beforehand and to be prepared to discuss your opinions in a concise manner. We feel that the informal round-table discussion will help serve this purpose. In that vein, it would be helpful if you could bring with you a copy of a few key references/data to support your opinions and plan to leave them with EPA for use in preparing the workshop summary report.

As illustrated in the attachment entitled "Discussion Sessions," there are a wide variety of questions to be answered. EPA recognizes that definitive answers are certainly not available to every question. The hope is that your combined experiences, expertise, and insights will help EPA formulate an effective research program to get answers to the critical questions. We look forward to seeing you next week and hope that the two days will be productive and informative to everyone.

Sincerely,

Joseph A. McSorley
Combustion Research Branch (MD-65)

EPA
N_2O Workshop
February 13 and 14, 1986

OBJECTIVE: To draw on a broad base of expertise to identify and prioritize R&D needs related to global N_2O combustion source emissions and control technologies.

Tentative Agenda
DAY 1

Thursday Feb 13, 1986

8:30 - 8:40	Welcome	R. P. Hangebrauck
8:40 - 8:50	Introduction	R. E. Hall
8:50 - 9:00	Purpose of Workshop	J. A. McSorley/W. S. Lanier
9:00 - 9:30	Global view of N_2O and O_3	D. Tirpak/M. Cavanaugh
9:30 - 12:00	SESSION I: N_2O SAMPLING & MEASUREMENTS	
9:30-10:15	A. Sampling	R. Weiss
10:15-10:30	BREAK	
10:30-11:30	B. Measurements	R. Weiss
11:30-11:45	Summary and Prioritization of Session I Issues & R&D Needs	
11:45-12:00	Completion of Session I Worksheets by Participants	
12:00 - 1:15	LUNCH	
1:15 - 4:30	SESSION II: N_2O FORMATION MECHANISMS	
1:15-2:30	A. N_2O Combustion Mechanisms Discussion Leaders	J. Wendt & W. S. Lanier
2:30-2:45	BREAK	
2:45-4:00	B. Appropriate N_2O Evaluation Ratios Discussion Leader	S. Wofsy
4:00-4:15	Summary and Prioritization of Session II Issues & R&D Needs	
4:15-4:30	Completion of Session II Worksheet by Participants	

N_2O WORKSHOP
February 13 and 14, 1986
Tentative Agenda

DAY 2

Friday Feb 14, 1986

8:30 - 12:00		SESSION III: N_2O SOURCE PRIORITIZATION
	8:30-10:00	A. Mobile Sources: Discussion Leader J. Sigsby
	10:00-10:15	BREAK
	10:15-11:30	B. Stationary Sources: Discussion Leader C. Castaldini
	11:30-11:45	Summary and Prioritization of Session III Issues & R&D Needs
	11:45-12:00	Completion of Session III Worksheet by Participants
12:00 - 1:30		LUNCH
1:30 - 3:45		SESSION IV: N_2O COMBUSTION CONTROL APPROACHES Discussion Leaders R. E. Hall/J. A. McSorley
	3:00-3:15	BREAK
	3:15-3:30	Summary and Prioritization of Session IV Issues & R&D Needs
	3:30-3:45	Completion of Session IV Worksheet by Participants
3:45 - 4:00		Completion of Overall Workshop R&D Needs
4:00		ADJOURNMENT OF WORKSHOP

Appendix C

INFRARED MEASUREMENT METHODS FOR NITROUS OXIDE

by

James W. Elkins

NOAA

Mark Zahniser

Aerodyne Research

Nitrous oxide (N_2O) is a strong absorber of infrared radiation (IR). Vibrational transitions in the energy levels of the molecule cause an absorption band which is composed of fine structure due to rotational transitions called absorption lines. The strongest band, ν_3, is centered near 2225 cm^{-1} (or 4.5μ), but is situated between the strong ν_3 band of carbon dioxide (CO_2) at ~2350 cm^{-1} and the 1-0 band of carbon monoxide (CO) at ~2150 cm^{-1}. Another band, ν_1, is located at ~ 1290 cm^{-1} near the ν_4 band of methane (CH_4), but is seven times weaker than the ν_3 band.

Measurement of N_2O by IR absorption techniques is possible using one of three commercially available instruments: tunable diode laser (TDL), Fourier transform infrared (FT-IR) and non-dispersive infrared (NDIR) spectrometers. The choice of analytical instrument is based on the experimental conditions, skill of operators, the concentration range of N_2O measured, the required precision and the potential for interferences from other IR absorbers, for example CO_2, CO, CH_4, and H_2O. A major advantage of infrared absorption compared to gas chromatographic techniques is the real time nature of the method. Instruments can be designed to give continuous, on-line monitoring of combustion streams or ambient gases. This makes IR absorption an attractive method for experimental systems which require fast response to changing conditions.

The tunable diode laser (TDL) spectrometer is extremely sensitive to N_2O with a minimum detection limit of ~ 500 ppt (10^{-12}) using 100 meter multipass gas cell or White cell. Signal processing of the direct IR absorption signal (by taking the second harmonic or derivative of this signal) is required for precise measurement of ambient concentration levels (~300 ppb). The optimum pressure for analysis is 10 torr, but measurements of N_2O are possible at 1 atmosphere. The narrow instrumental linewidth of the TDL, which can be <0.0002 cm^{-1}, can resolve the line width of individual rotational lines in a band at pressures of 10 torr. Precisions of ± 0.5% at ambient concentration levels of 300 ppb (parts per billion) are possible. Interferences by other IR absorbing gases can be eliminated by tuning the operating current of the diode to another line away from the interfering line. The typical tuning range of the TDL is about 50–100 cm^{-1}. Measurements of IR absorbing gases by the TDL using 2nd harmonic detection are linear over an order of magnitude; and the dynamic range can be improved by generating a calibration curve using a wide range of standards. The cost of a typical diode laser spectrometer with gas handling accessories is about $50–75K. The TDL itself costs about $1–2K and has a lifetime between 1 and 2 years.

The main advantages of the TDL are its high spectral radiance, narrow linewidth and range of tunability which make it a superior light source compared to blackbody based methods. The main disadvantages, however, are the degree of variability from diode to diode with respect to multiple mode structure, limited tuning range and the wavelength reproducibility. These factors restrict present TDL usage to research applications which require fairly skilled operators. Another disadvantage is the expense which is presently dominated by the low operating temperature required. The low temperatures necessitate closed cycle liquid helium cryogenic coolers which

cost between $20K and $80K. Advances in laser diode technology, however, may remove this restriction. Higher temperature diodes that operate above 77K and can be cooled by less expensive liquid nitrogen cryostats are currently being developed. Future advances in the overall reliability of TDL's may lower the total operating cost substantially.

Fourier transform infrared (FT-IR) spectrometers are versatile instruments which are capable of measuring more than one IR absorbing gases at a time over a large frequency range (typically 400 to 4000 cm^{-1}). The resolution of the FT-IR spectrometer can be varied by changing the path difference between the moving and fixed mirrors. A resolution of 0.12 cm^{-1} is sufficient for most gases. FT-IR spectrometers are not as sensitive as the TDL spectrometers, but, with a pathlength of 100 meters in a White cell, detection limits of <50 ppb are possible. At 0.12 cm^{-1} resolution, samples can be processed in less than 1/2 hour. Precisions of 1% are possible with this amount of accumulation time.

The optimum pressure for analysis is 1 atmosphere. Lower pressure (10 to 100 torr) analysis requires knowledge of line broadening parameters since the instrumental resolution is insufficient to resolve the line width. The typical cost of the FT-IR spectrometer and gas handling accessories (including White Cell) is between $35K and $60K. Interferences by other gases may pose a problem, but, in most cases, interfering gases can be digitally subtracted using reference spectra. One advantage of the FT-IR spectrometer is a time resolved feature that permits microsecond resolution of changing gas concentrations during a reproducible chemical reaction (i.e. flash photolysis), although the overall sensitivity is reduced in this mode.

Non dispersive infrared (NDIR) spectrometers are low cost ($15 to 20K) instruments capable of measuring ppm levels continuously at precisions <1%. Interferences from CH_4, CO, and CO_2 may result in large errors to the measurement of N_2O concentration in combustion samples. These errors may be reduced by the appropriate selection of an optical filter. The NDIR spectrometer is non-linear at concentrations below 5 ppm. Measurements below 5 ppm will require research and development of an NDIR instrument that is not currently available from commercial suppliers. Some research funds should be set aside to improve the sensitivity and to reduce the errors of interfering gases.

TABLE 1

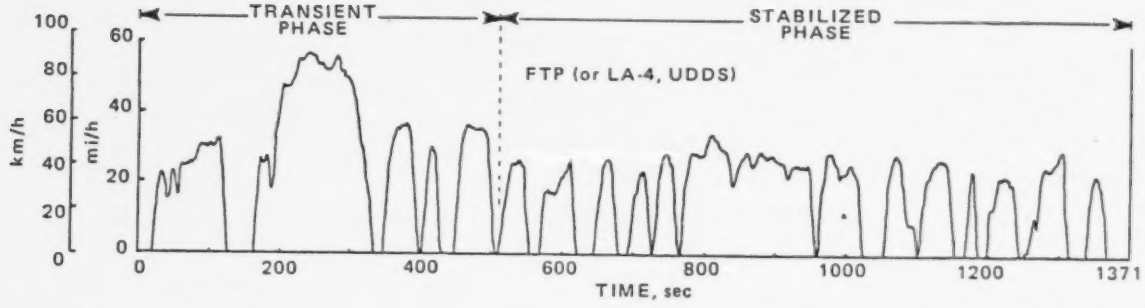
Comparison of IR Instruments

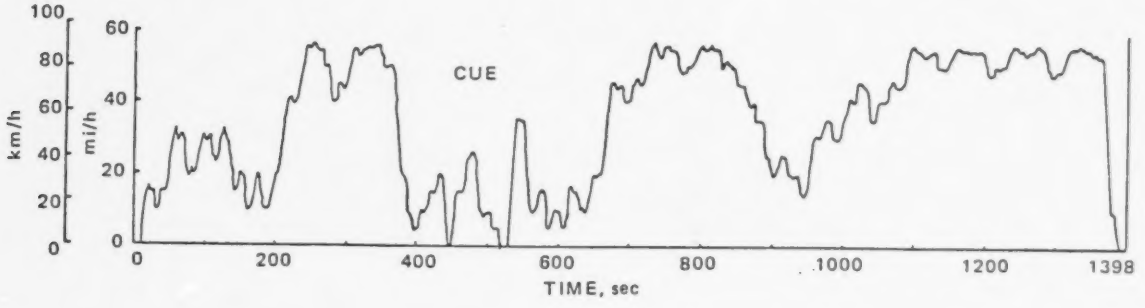
In Measuring N_2O Concentration

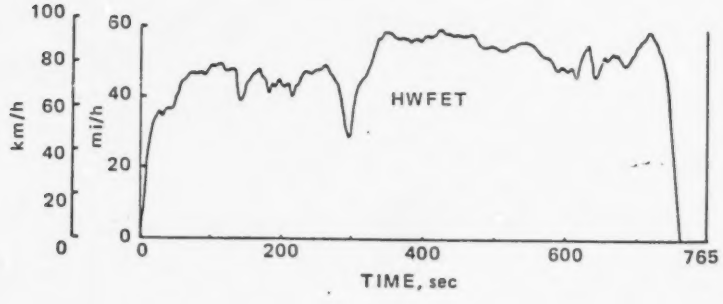
	TDL	FTIR	NDIR
Precision	± 0.5%	1%	1% high conc. ± 5 to 10% low conc.
Levels	10 ppb up	50 ppb up	5 ppm up
Optimum Pressure	10 torr	760 torr	760 torr
Sample Rate	3 msec	1/2 hour	continuous
Sample	White Cell	White Cell	15 cm cell
Linearity	10	10	10 problem at low conc.
Cost with auxiliary gas handling equip.	$50-75K	$35-60K	$15-20K
Advantages	Kinetic studies ratio low level sensitivity	many gases Kinetic studies	inexpensive
Disadvantages	White Cell $2K/diode Cryogenics	White Cell	non-linear at low concentrations sensitivity

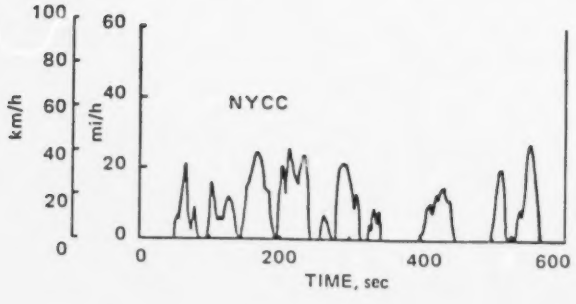
Appendix D

Time Traces of Various Driving Schedules









Time Traces of Various Driving Schedules (Continued)